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**ROYAL SOCIETY OF LONDON**

**SERIES A**

**CONTAINING PAPERS OF A MATHEMATICAL AND  
PHYSICAL CHARACTER.**

**VOL. LXXXI.**

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PROCEEDINGS OF  
THE ROYAL SOCIETY.

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SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

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*A Tantalum Wave-detector, and its Application in Wireless  
Telegraphy and Telephony.*

By L. H. WALTER, M.A.

(Communicated by Dr. J. A. Ewing, C.B., F.R.S. Received April 23,—  
Read May 7, 1908.)

It has been known for some years that the metal mercury lends itself well to the purpose of constructing a detector of electric oscillations which is capable of spontaneously returning to its initial or sensitive condition, or, in other words, is spontaneously decohering. The two elements which have hitherto been known to show this property when used in conjunction with mercury are iron (steel) and carbon. Both of these have been employed, singly or together, in the Italian Navy coherer, otherwise known as the Castelli or also the Solari coherer.

The use of carbon is, however, very undesirable for reasons which are well known, while iron is a very unsuitable metal for use in places where there is any considerable amount of moisture in the air;\* at the best it is only a question as to how long rusting can be deferred.

These considerations had, as early as 1902, led the author to consider means for utilising a noble metal in combination with mercury. It was at that time found impossible to make use of platinum without the employment of some liquid dielectric—in this case pure water—interposed between

\* Fleming, 'Principles of Electric Wave Telegraphy,' p. 371.

the mercury and the platinum, and then only when the platinum wire was glass-sheathed. Such an arrangement required, in addition, to be mechanically restored to the sensitive state.\*

The recent trend of work in wireless telegraphy has all been in the direction of the employment—at least for general use—of telephonic or aural reception, and hence coherers have mostly fallen into disuse, especially as the only reliable and durable ones were those which required mechanical restoration.

The advent of the tantalum lamp, which appeared to promise that this hitherto unobtainable metal would soon be commercially available, seemed to hold out some possibility of successfully overcoming the previous difficulties in the way of finding a suitable noble metal. For the fact that tantalum is a noble metal in so far as its chemical behaviour is concerned; that it is indifferent to atmospheric influences; that it has great strength and ductility; and, finally, that it is absolutely indifferent to mercury, seemed to bear out the above view. The chemical and physical properties of tantalum have been fully dealt with by von Bolton and by von Pirani, and owing to the importance of the metal in the incandescent lamp industry these have become fairly generally known.

One difficulty presented itself at the outset, in that it was impossible at that time (whatever may be the case at present) to obtain even the smallest quantity of the metal in any other form than fine wire as is used in the tantalum lamps. It was, therefore, necessary to try whether under the apparently unfavourable conditions which the use of the metal in such a form imposed any wave-sensitive effect could be observed when used with mercury.

A first experimental detector was made by passing two tantalum wires, taken from an ordinary tantalum lamp, down two fine glass capillary tubes, and allowing the wires to project about  $1/20$  inch, and their points to just touch the surface of a small pool of mercury. The sensitiveness of the metal to heating when in the state of fine wire made it impossible to solder joints satisfactorily, and so in later forms the tantalum wire was held in a minute clip hammered out at the end of a stouter platinum wire.

Trials of this detector gave remarkable and unexpectedly good results. It was found that both the liquid dielectric and the insulating sheathing could be dispensed with and yet a perfect spontaneously restoring detector be obtained, and one that, while exceedingly sensitive, gave signals which are notable for their loudness and pure tone. Further, the mercury surface could be made as large as was desirable, with benefit to the sensitiveness, as

\* Prasch, 'Sammlung elektrotechnischer Vorträge,' vol. 6, p. 254.

opposed to the case of the Italian Navy coherer, where it is only by the artificial augmentation of the surface tension of the mercury relatively to its mass (*i.e.*, by reducing the diameter of the mercury globule) that the spontaneous restoration is rendered at all possible.

It was soon found that better results could be obtained with a single tantalum point, provided this was connected to the negative pole of the potentiometer arrangement, the best applied voltage being apparently 0.2 to 0.4 volt.

The general construction and actual size of the detector as now used is shown in section in fig. 1, the whole arrangement being hermetically sealed in a glass bulb.

Here P is a sealed-in platinum wire, forming one terminal, dipping into a small pool of mercury M, in the glass vessel G; the other terminal is also a platinum wire P<sub>1</sub>, having a clip at its end, holding a short length (3/16 inch about) of tantalum wire T of 0.05 mm. diameter. The sealed-in platinum loops form a handy means of connecting up, with the aid of a lamp-holder of the Swan type. Before sealing up, mercury is poured into the bulb, through a small side neck N, to such a level that the tantalum point is just immersed, which is best ascertained experimentally by the sound in the telephone receiver. The bulb can then be sealed, having previously been exhausted, if so desired. When properly constructed such detectors are permanent, and do not deteriorate apparently, at any rate over a considerable number of months, which is as long as they have been available up to the present.

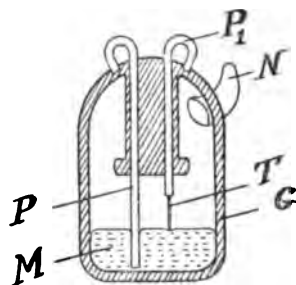


FIG. 1.

To guard against accidental breakage of the fine wire point, three such wires are now generally held in the clip, two being turned up out of the way; either of these can at any time be bent down into the mercury by means of a wire inserted after opening the sealed neck, the bulb being then resealed. For this reason the bulbs are preferably left unexhausted.

The author has carried one of these detectors about in his coat pocket and in a hand-bag to France and other places, and after seven months the fine point is absolutely unmoved from its original position, in spite of the hundreds of times the half ounce or so of mercury in the bulb has been jolted about. This disposes of any idea that the point arrangement is at all fragile.

Detectors of this form have been tested at actual wireless telegraph stations, and it has been found that, while possibly not so sensitive for very weak oscillations (signals) as the electrolytic or magnetic detector, for



slightly stronger oscillations the sound is *several times louder* than that obtained with the electrolytic, which is itself much more sensitive than the magnetic detector, and these results were obtained when each (the tantalum and the electrolytic) detector had the telephone most suitable for it. With the same telephones as are supplied with the "Telefunken" apparatus for use with the Schloemilch electrolytic detector, and consequently not so suitable for the tantalum detector, the signals obtained when the latter replaced a new Ferrié electrolytic detector were several times louder. (It is notoriously difficult to estimate telephonic sounds quantitatively, but the signals can be described as "good readable" and "loud" in the case of the electrolytic and the tantalum detectors respectively.) With the second detector made, very loud signals were obtained at a distance of 70 miles over sea, without any attempt at tuning, louder than those obtained with the electrolytic detector with the aid of a step-up oscillation transformer and careful tuning. Using one of the less satisfactory of the later models of the tantalum detector, loud commercial signals have also been obtained at a distance of 450 miles, the transmitter in this case not being one of the high-power stations, which are but poor tests, but an ordinary 2-kilowatt ship installation. The signals were in this case only slightly less loud when the tantalum detector replaced the electrolytic detector in the circuit, and since the very high resistance telephones used were not suited to the tantalum detector, it is clear that the latter may be regarded as on practically an equal footing with the electrolytic detector, provided the signals are not too weak.

The apparent want of sensitiveness for very weak signals is due to the slight hissing sound which is normally present in all such imperfect contacts, with mercury especially, though it is on a reduced scale as compared with the Italian Navy coherer.

An examination of the tantalum detector by the resistance substitution method shows that in the receptive condition these have a fairly low resistance, 1200 to 1800 ohms (as compared with the filings coherer, 100,000 ohms or so; and the electrolytic detector, 30,000 to 50,000 ohms). This low resistance should prove beneficial to the tuning in certain cases. When oscillations are acting, the resistance drops to anything from 250 ohms for strong to 70 ohms, say, for very strong signals. The great loudness of the signals obtainable with the tantalum detector is due to the large change in the current through the telephones. For this detector the ratio of the current when oscillations are acting to that in the normal condition ranges from 3:1 to 8:1, and can amount to 30:1 without reaching the maximum sound obtainable; the normal current, using 580-ohm telephones, is about 1/20 to 1/10 milliampere.

For the purpose of comparison the same ratio has been measured for a coherer of the Italian Navy type. This gave a current ratio of 3 : 1 (about) as a maximum, above which it cohered permanently; it was more usually 3 : 2, at least in the author's experiments. \* The results with an electrolytic detector were not satisfactory, so that it is preferred to quote Reich's statement,\* that this ratio can easily reach 10 : 1.

It will thus be seen that the electrical behaviour of the tantalum detector approximates more to that of the electrolytic detector, as also does the sound.

Although the resistance of the tantalum detector is low, there is little likelihood of the point being damaged, for, unlike the case of a solid metal-to-metal contact, a welding of the contacts is excluded, and no case has been observed in which it has been possible, with very powerful oscillations, to prevent the spontaneous return to the decohered state.

In spite of the fact that, as shown, the tantalum detector is a sensitive, useful, and long-lived receiver for wireless telegraphy, it is, in the author's opinion, not so specially suited for this purpose as for the closely-related branch of signalling—wireless telephony.

For this more recent application of electric wave propagation the use of microscopically weak signals—such as are at present so favourably regarded in some quarters for the purpose of covering long distances with a minimum amount of power and, probably, of enhancing the possibility of tuning out—is obviously out of the question, and here it is that the superiority in loudness of the tantalum detector for moderately strong oscillations comes in. This is particularly the case owing to the fact that the electrolytic detector, which has been most generally used for wireless telephonic purposes up to the present time, cannot claim to be quite satisfactory as regards tone, reproduction of speech being rather harsh and metallic. It further, as Tissot has lately shown,† very soon, with quite moderately weak oscillations, reaches its maximum of loudness, and beyond this all additional energy is wasted, since it contributes nothing to the loudness. The harshness has been referred to by de Forest, who now uses for wireless telephony his adaptation of Fleming's "oscillation valve," which he has for some reason renamed the "Audion." The life of such a detector is, however, very limited, being determined by that of the lamp filament employed; it is unlikely that this will amount on the average to more than 800 hours.

The form of detector just described, while serving very well for use in fixed stations where a firm support can be obtained, is not so satisfactory when

\* 'Physikal. Zeitschr.,' vol. 5, p. 338, 1904.

† 'Comptes Rendus,' vol. 145, p. 226, 1907.

the detector is liable to be subjected to shaking or mechanical shocks during the reception of messages. Of existing forms of detector there are several which are rather sensitive in this way, and since a detector capable of withstanding rough usage may be useful in certain cases, it was thought desirable to find some method of immobilising the mercury while not interfering unduly with the sensitiveness to electrical stimuli or with the loudness of tone. Various devices have been tried without success, but one satisfactory solution is arrived at by constructing the detector in the following manner:—The tantalum wire is fastened in a platinum clip and the end of the tantalum encased in glass by a special method, necessitated by the impossibility of sealing-in tantalum in the ordinary way as is done with platinum. The platinum wire is sealed into a minute glass bulb B (see

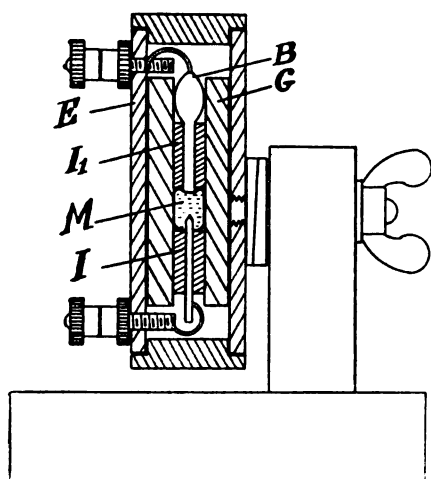


FIG. 2.

fig. 2) blown on one end of a glass tube; the other end of the tube is connected to an air pump and the interior exhausted. The glass tube is next heated, when the vacuum causes it to collapse on to the tantalum wire. The end of the glass-sheathed wire can then be ground down so that the tantalum surface is just flush with the glass (simply breaking off the glass end usually suffices). The mercury is contained in a glass tube G, having a bore of  $5/32$  inch. A larger tube would be better, but the sensitiveness to shaking then reappears; a smaller tube gives a less sensitive and more

variable detector. An ivory plug I, through which a platinum or nickel wire passes and projects, is placed at one end of a length of a few inches of such glass tube with thick walls. A few drops of mercury—enough to form a pellet (M) about  $5/16$  inch long—are then put in and a second ivory plug  $I_1$ , this one with the sheathed tantalum wire passing through it and projecting about  $1/20$  inch, inserted so that the tantalum glass surface just dips into or under the mercury surface. The best (most sensitive) position is that shown in fig. 2, with the glass tube vertical and the tantalum electrode at the top, and this gives a detector which may be roughly shaken or tapped during the reception of signals without affecting their sound in any way. For sealing up, the whole arrangement is encased in an ebonite tube E, and the ends filled in with insulating compound. The device is then

permanent, though experience (time) is wanted to decide whether it is as inalterable as the first form.

As it seemed somewhat remarkable that such exceedingly good results should be obtainable with tantalum, the first metal tried, a series of experiments was carried out, using mercury in conjunction with other metals hitherto untried by the author, especially those which are most resistant to the action of mercury.

In the case of the metals iron, steel, nickel, and tungsten, and "Eureka" resistance alloy, the metal was obtainable in the form of fine wire, and was used as a point just impinging on the mercury surface in exactly the same way as with the tantalum point. But with all these metals it was quite impossible to obtain anything but a "perfect" contact, even when the mercury was reduced to a quite small globule and the applied potential difference was reduced to a very low value, 0.1 volt or less. The tungsten here was not, perhaps, perfectly metallic, being that taken from an "Osram" and from a tungsten-zirconium lamp. Trials were also made with the so-called "high-resistance" tantalum wire, *i.e.*, wire which has been nitrogen-treated after the method described by the General Electric Company of America—a matter which has formed the subject of a previous note by the author.\* In this case, also, no imperfect contact effect was observable, although the resistivity of the material was four times as great as that of the pure metallic tantalum. The other metals tried were only available in the massive form, but were used with as fine a point as it was possible to get, dipping into mercury as before. No effect was obtained with vanadium, molybdenum, cobalt, manganese, tellurium, zirconium, ferro-silicon, ferro-manganese, ferro-nickel, nor with antimony or bismuth: all these metals, except possibly molybdenum and zirconium, give a "perfect" contact.

Trying pure tantalum with different solid metals, it was found that a sensitive and moderately loud spontaneously restoring detector can be made by placing a tantalum point so that it bears on an iron surface (best oxidised). An equally sensitive but not quite so loud detector is obtained with a similar arrangement, but using tantalum and tellurium. Since both these latter metals are unaffected by the atmosphere, such a device might prove of value in the laboratory, for intermittent use for instance. A very weak effect was observed with cobalt, antimony, manganese, and bismuth in this order of decreasing loudness, while with molybdenum and vanadium there was no effect whatever. But with all these coherers one has only to compare

\* 'Electrician,' vol. 60, p. 199, 1907.

them with the tantalum point dipping into mercury to realise that they are hopeless as practical competitors.

It will thus be seen that, so far from this property of imperfect contact and spontaneous decoherence with mercury being common to several metals, the behaviour of tantalum is apparently unique, while the effect obtained greatly surpasses that observed with iron. This latter has hitherto been considered the only possible metal for use in this connection; but it has been shown above that the property possessed by iron has to be artificially aided before it can even begin to serve the purpose which can now be more effectively carried out by a noble and inalterable metal.

In conclusion, it is interesting to note that, by a suitable choice of material, the primitive simplicity of the single-point contact between two metals can be reverted to and yet practically all the attributes—speed, positive decoherence, loudness, long life, and non-exposed parts—which are required of the modern detector be retained.

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### *Seleno-Aluminium Bridges.*

By Professor GEORGE M. MINCHIN, M.A., F.R.S.

(Received April 28,—Read May 7, 1908.)

A seleno-aluminium bridge consists of a very thin and narrow layer of conducting selenium connecting two surfaces of aluminium which are separated by an insulator, such as glass or mica. The bridge may have a linear or a circular form. If the first, it is made thus: let P and Q be two strips of aluminium separated by a very thin plate of mica SS; the whole, as we look at the figure, forms a perfectly plane surface. If the plates P, Q are connected with a galvanometer G and a battery B of a few cells, no current passes because of the insulation of the mica; but if we smear a thin layer of melted selenium over the surfaces of the plates, and, of course, over the mica, and then heat this layer in the well-known way until the selenium assumes the brownish grey modification which conducts a current, the narrow space of mica insulation is bridged over by a conductor, and the current of the battery passes.

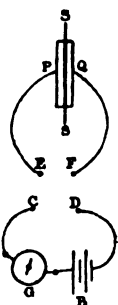


FIG. 1.

This bridge will have a certain conductivity in the dark, and that conductivity, as we shall see, will depend on the voltage of the battery B. If light—even the feeble light of a distant candle—is allowed to fall on the face of the bridge, the conductivity is very much increased, and the galvanometer will show a much increased current.

The bridge has no definite resistance (or conductivity) because it is different for different voltages of the applied battery, and, of course, much depends on the extent of the surface of the mica separator; but, roughly speaking, it will be in the neighbourhood of 40 or 50 megohms if the length of the plates P, Q is about a centimetre and the thickness of the mica about 0.01 mm. The galvanometer G should be a sensitive D'Arsonval dead-beat one.

The circular form is made by boring a cylindrical hole through a thick rod of aluminium, placing in this hole a tightly-fitting thin glass tube, and forcing into this glass tube a tightly-fitting rod or wire of aluminium. The surfaces of aluminium tube, glass tube, and aluminium wire are worked quite plane, and selenium is then (as above) smeared over them so as to bridge across the glass separator. Thus the outer aluminium tube and the inner aluminium rod or wire take the places of the two plates P, Q in the above figure. If the diameter of the glass tube is about 0.5 mm., the image of a star can be focussed



on the little ring, or bridge, of selenium, and the light of the star will alter the conductivity of the bridge and give an increased deflection on the galvanometer scale.

If the linear bridge is used, we can place the thin line SS of the bridge in any part of the spectrum of the star and obtain the deflections caused by lights of various colours or wave-lengths.

As indicated in the figure, one pole of B is always connected with a fixed pole of the galvanometer, while the poles E and F of the bridge can be connected, respectively, either with C and D (the second poles of the galvanometer and battery) or with D and C. It is thus seen that the battery current always passes through the galvanometer in the same sense, but that the sense in which it passes through the bridge can be varied.

Before we answer the question: how does the change of conductivity of the bridge (or the deflection on the galvanometer scale) depend on the intensity and the colour of the incident light? we must find how the employment of different voltages in the battery B affects the results. To determine this, I connected the bridge successively with batteries of 2, 4, 6, 8, 10, and 12 volts, and the following are the numbers representing the corresponding current strengths indicated by the galvanometer: 35, 104, 203, 367, 558, 793. Each of these currents took a considerable time to establish itself—roughly from 20 minutes to half an hour. The effect is a gradual one. Dividing the currents by the corresponding voltages, we have for the corresponding conductivities the numbers: 17.5, 26, 36, 46, 56, 66. Thus *the conductivity is not constant, but is a function of the voltage.*

The accompanying figure (fig. 2) represents as ordinates the currents and the conductivities corresponding to the voltages.

The curve at the left of the figure is the diagram of current-strengths produced, when the bridge is in the dark, by different voltages, while that at the right represents the corresponding conductivities of the bridge, and we may, I think, accept this latter as a right line. Thus, if  $V$  is any voltage and  $c$  the corresponding conductivity,

$$c = kV + K, \quad (1)$$

where  $K$  is the conductivity, represented by the ordinate of the point A, when an infinitely small voltage is applied. This  $K$  can be regarded as the *intrinsic conductivity* of the selenium. If  $C_0$  denotes the final current produced by any voltage  $V$ , the curve at the left is a parabola, since  $C_0 = cV$ , or

$$C_0 = V(kV + K), \quad (2)$$

which denotes a parabola whose vertex is at the left of the axis of current and below the axis of voltage.

To determine the law of variation of current with the intensity of light, I used the spectrum of a Nernst lamp, placing the bridge at distances 6, 5, 4, 3, 2, and 1 metres from the source, the bridge being slid up the inside of a very thick cylinder of cardboard blackened on the inside; but this was not found to be a very convenient arrangement, so I finally confined the observations to two coloured lights—one a pure red, and the other a very nearly pure blue. These lights were produced by passing the light of the Nernst lamp through solutions of fuchsine in water and sulphate of copper in ammonia.

If  $R_0$  is the resistance of the bridge in the dark for a given voltage, and  $R$

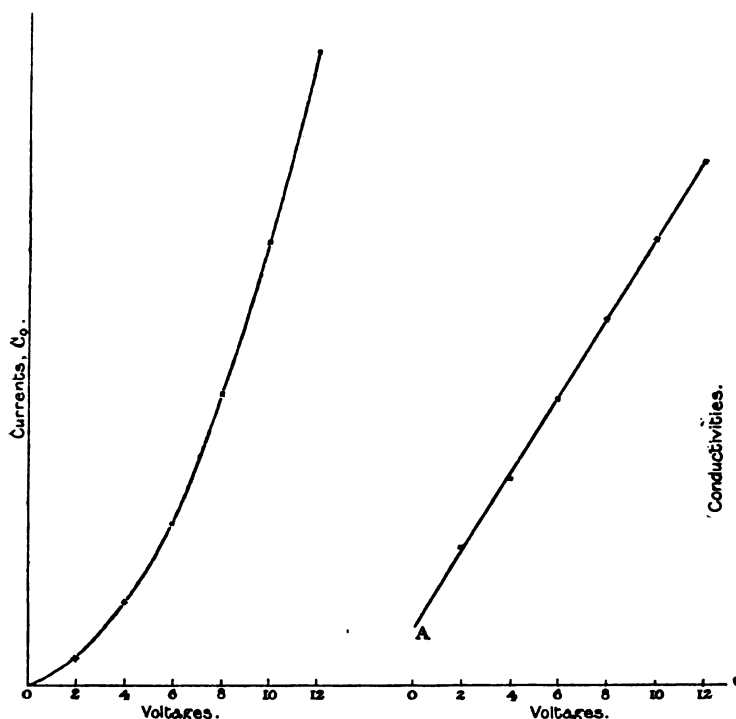


FIG. 2.

its resistance when light of intensity  $i$  falls on it, the fraction  $(R_0 - R)/R_0$  suggests itself as a quantity whose connection with  $i$  might be determined; but there is no very simple function of  $i$  which measures this quantity. After many trials, I found the following to be a relation which is very fairly accurate:—

Let  $i_1$  be the intensity of light of a given wave-length, which alters the current  $C_0$  into  $C_1$ , and  $i$  the intensity of the same light, which alters  $C_0$  into  $C$ ; then

$$\log \frac{C}{C_0} = \left( \frac{i}{i_1} \right)^n \cdot \log \frac{C_1}{C_0}, \quad (3)$$

It does not matter what the voltage of the auxiliary battery B is, the ratio  $C/C_0$  is practically the same. Of course, the  $C_0$  corresponding to a voltage of 6 is much greater than the  $C_0$  corresponding to a voltage of 2, but so is the C produced by a given light greater with the first voltage than with the second.

The light of the Nernst lamp was made to pass through a rectangular glass trough filled with water, so that the heat rays might be cut off; from this trough it passed through a thin glass trough containing the coloured liquid; and thence it was passed through a series of thick cardboard cylinders, each 1 metre long and 1 decimetre in diameter. These cylinders were blackened on the inside and placed end to end, so that we could use a cylindrical tube varying in length from 1 metre to 6 metres. The selenium bridge was placed at one end of this tube, and was, of course, completely screened from all light, except that of the Nernst lamp.

The focus from which the central rays of the incident light could be considered to emanate was about 14 cm. from the end of the tube, so that the distances of the luminous point from the bridge, with successive lengths of tube, were approximately 1·14, 2·14, 3·14, 4·14, 5·14, and 6·14 metres.

The following table shows the values obtained for  $C/C_0$  at the various distances employed for the red and blue lights, the battery employed with the first having a voltage of 2, and with the second a voltage of 4:—

Distances .....	6·14.	4·14.	3·14.	2·14.	1·14.	
$C/C_0$ , red .....	1·83	2·13	2·33	2·83	4·27	2 volts.
$C/C_0$ , blue .....	1·205	—	1·355	1·484	1·875	4 volts.

Applying equation (3) to red light at distances 6·14 and 1·14, we have

$$\log 1·83 = \left(\frac{114}{614}\right)^{2n} \cdot \log 4·27,$$

since the intensities are inversely as the squares of the distances. This gives  $n = 0·262$ . Similarly for the other distances employed, and the values of  $n$  which we find are successively

$$0·262, \quad 0·253, \quad 0·266, \quad 0·264.$$

For the blue the values are

$$0·361, \quad 0·359, \quad 0·369.$$

The mean value for the red may be taken as 0·26, and that for the blue 0·36.

The accompanying figure shows two curves whose ordinates are the values of  $C/C_0$  for the red and blue, the abscissæ being the intensities of the light.

The larger the voltage of the auxiliary battery B, the larger will be the values of  $C$ ; but the value of  $C/C_0$  for a given intensity and colour is found to be the same whatever the voltage.

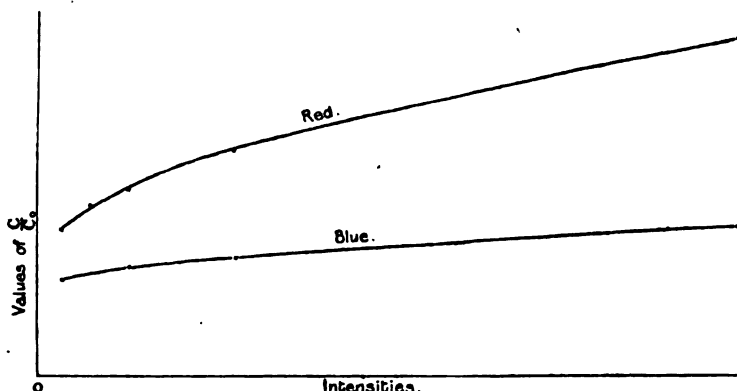


FIG. 3.

The red light belonged to that part of the spectrum in the neighbourhood of the ray B, and the blue to the portion about midway between F and G. If we take the ratio of the wave-lengths in these parts of the spectrum as roughly equal to 64:41 and compare this with the ratio of the index  $n$  in equation (3) for the blue to the value of  $n$  for the red—namely 36:26—we find the two ratios not very different. This suggests that  $n$  is inversely proportional to the wave-length, and that equation (3) may be written in the form

$$\log \frac{C}{C_0} = \left( \frac{i}{i_1} \right)^{k/\lambda} \cdot \log \frac{C_1}{C_0}, \quad (4)$$

where  $k$  is a constant depending merely on the selenium bridge employed.

In constructing these bridges I have found it desirable to coat the selenium layer with a very thin layer of melted paraffin. A small piece of paraffin laid on the face of the bridge while it is yet hot is spread over the selenium with a hot glass rod. This paraffin gives the surface of the grey layer of selenium a blackish appearance, but does not in the least diminish its sensitiveness to light. It is just possible that it rather increases the sensitiveness. At any rate, it protects the selenium from the action of vapour in the air, and it seems to facilitate the return of the bridge to its natural state when the light is withdrawn.

I must now mention a very strange peculiarity of the bridge, of which

I have no explanation. It is that after exposure to light *its resistance to a current traversing it in one direction is not the same as to a current traversing it in the opposite direction*. The difference in the resistances to currents flowing through the bridge in opposite directions was sometimes found to amount to more than 30 per cent. with a voltage of 6. This would seem to imply a residual electromotive force in the bridge after the light is withdrawn, so that the bridge becomes a "cell," and not a mere resistance; but this is not so: when we seek for a deflection due to the bridge alone (by cutting off the battery), we find no deflection whatever.

Also, when the light is withdrawn the return of the bridge to its natural state (or of the spot on the scale to its initial position) is very much accelerated by reversing the current through the bridge several times and then breaking the circuit.

Two of the facts which I have given above—namely, that the resistance of selenium to a current is not independent of the voltage of the battery employed, and that its resistance is not the same to two currents traversing it in opposite directions—were new to me when I observed them in the course of these experiments; but Dr. Shelford Bidwell pointed out to me that both facts were discovered previously by Adams and Day. Their paper on selenium "cells" (more properly *resistances*) is in the 'Phil. Trans.' for 1877; and, on examining it, I find some observations which do not agree with what I have found for seleno-aluminium bridges. Adams and Day used a thin plate of crystalline selenium 5.4 cm. long, 1.2 broad, and 0.08 thick, with platinum wires fixed into it and its ends.

I always use aluminium and not platinum, because when working with selenium *cells* (in which a voltage is generated) I found much greater sensitiveness with aluminium than with platinum.

Adams and Day found that when this plate was inserted in the circuit of a battery and galvanometer, as in fig. 1 above, the longer the current was allowed to flow the *greater* became the resistance of the selenium. This is precisely the reverse of what I have observed, and it seems to point to some chemical action at the electrodes.

Owing to this, they never allowed the current of the battery to pass through the plate for more than 15 seconds, so that they could not have obtained the result given in equation (1) above; for the *final* value of the conductivity of a bridge is attained after a time very much greater than 15 seconds.

Another notable difference in the results is this: Adams and Day, using exposures of 10 seconds, found that the change of resistance produced by light "varies exactly as the square root of the illuminating power." For a considerable time I believed, from observation, that the *fourth* root of the

intensity was nearest to the truth; but I found that no such law agreed satisfactorily with experience. If  $\delta$  is the amount by which a resistance  $R_0$  (in the dark) is diminished by light of a given colour and intensity  $i$ , equation (3) above gives

$$\delta = R_0(1 - e^{-ki^n}), \quad (5)$$

where  $k$  is a constant, and  $n$  is a number depending on the colour of the light. This equation does not make  $\delta$  proportional to  $\sqrt{i}$ .

If  $i$  is comparatively feeble, and therefore  $\delta$  small compared with  $R_0$ , this equation makes  $\delta/R_0$  proportional to  $ki^n$ ; and since  $n$  is not very different from  $\frac{1}{4}$  for red light, the change of resistance is roughly proportional to the fourth root of the intensity.

A peculiarity of my seleno-aluminium bridges which must be mentioned is this: after the bridge has been in use for a considerable time (perhaps some months) its resistance for high voltages is extremely unsteady. Thus, a bridge which had been much used had a perfectly steady behaviour with 2 volts, but with 6 volts the spot on the scale moved with great suddenness over large distances, the bridge being all the time in the dark.

#### *The Time-current Curve.*

A very important question relates to the *time-current curve*, i.e., the curve whose ordinates represent the values of the current at different times during the exposure to light, the abscissæ being the corresponding times.

The following typical figures represent a time-current curve for red light and one for blue (fig. 4, p. 16).

The observations of the deflections on the scale were made at intervals of 15 seconds, and the values of the time,  $t$ , as multiples of this interval, are set off along the axis OT, while the values of the current are measured along OY. The points A,  $b$ , C, D . . . H represent the observations with red light, the voltage of the auxiliary battery being 4, and the distance of the radiant point of the light of the Nernst lamp from the bridge 2.14 metres (called roughly 2 metres in the diagram). The curve A', B', C' . . . similarly represents the results with blue light. Two different selenium bridges were used in these observations, and OA represents  $C_0$ , the current in the dark, in the first case, while OA' represents the  $C_0$  in the second case.

If the two bridges employed had been the same, the points A and A' would be the same; but they are sufficiently close to show the difference between the curves.

With red light at such a small distance as 2 metres the rise of the current at the instant of exposure of the bridge to the light is so rapid that no trust-



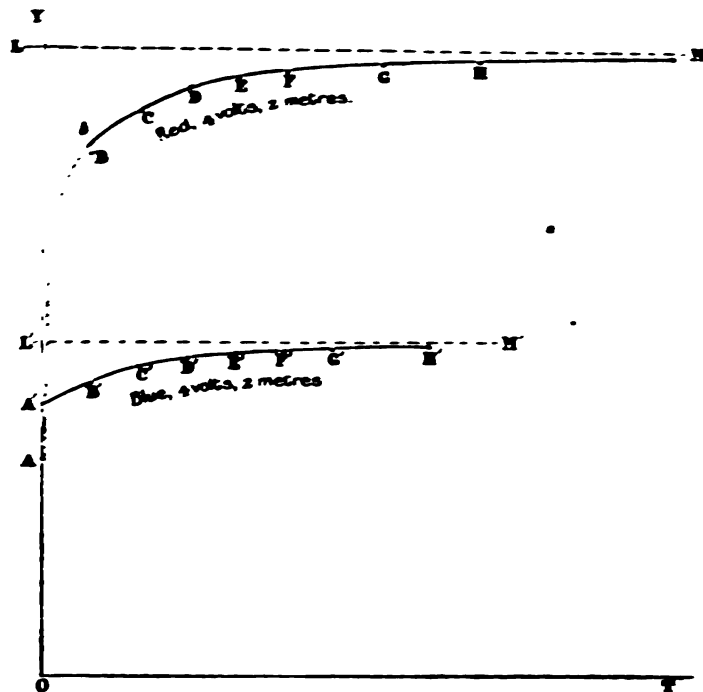


FIG. 4.

worthy observation of the deflection during the first 15 seconds—even with a D'Arsonval galvanometer, which is said to be “dead-beat”—can be made: the needle is too rapidly on the move, and even if its deflections were photographed, we could scarcely infer the current-strength from them, owing to inertia.

Hence the position of the point *b*, which represents an attempt at a reading at the end of the first 15 seconds, is quite untrustworthy.

Representing the interval of 15 seconds by  $\tau$ , and the current by  $C$ , the following were the actual readings with the red:—

$t$ .	0.	$\tau$ .	$2\tau$ .	$3\tau$ .	$4\tau$ .	$5\tau$ .	$7\tau$ .	$9\tau$ .	$13\tau$ .	$\infty$ .
C.....	54	130	141	147	149.8	151	153	154	155.3	156

(p)

the fractions of divisions being rough estimates.

For the blue the corresponding table is—

$t.$	0.	$\tau.$	$2\tau.$	$3\tau.$	$4\tau.$	$5\tau.$	$6\tau.$	$8\tau.$	$\infty.$
C .....	68	73	77	79	80.1	81	81.3	82	83

(β)

Both the voltage and the distance of the light from the bridge were varied in other experiments.

In the absence of a knowledge of the physical cause of the action of light on selenium, it is allowable to make a hypothesis which will accord with these observations and the curves representing them; and I therefore make the following plausible assumption:—

If  $C$  is the current-strength at any time  $t$  after exposure, and  $H$  the final value attained by  $C$ —represented by the height of the line  $LM$  in fig. 4 for red light—the time-rate of increase of  $C$ , viz.,  $dC/dt$ , should be proportional to  $H-C$ , or to some power of  $H-C$ ; that is, we assume that

$$dC/dt = k(H-C)^p, \quad (6)$$

which gives  $(H-C)^{-m} - (H-C_0)^{-m} = \lambda t, \quad (7)$

where we use  $m$  for  $p-1$  and  $\lambda$  for  $k(p-1)$ .

The quantities to be determined in this equation are  $H$ ,  $m$ , and  $\lambda$ ; and they can be theoretically found from three simultaneous values of  $C$  and  $t$ .

To see how such an equation satisfies the results, take the table ( $\rho$ ); discard the reading for  $t = \tau$ , since it is known to be untrustworthy, and take  $C_2$  and  $C_3$ , i.e., the values of  $C$  corresponding to  $2\tau$  and  $3\tau$ , at the same time using our knowledge that  $H = 156$ . We have then the equations

$$15^{-m} - 102^{-m} = 2\lambda\tau, \quad (8)$$

$$9^{-m} - 102^{-m} = 3\lambda\tau, \quad (9)$$

which give for  $m$  the equation

$$3(15)^{-m} - 2(9)^{-m} - (102)^{-m} = 0. \quad (10)$$

Of course, one value of  $m$  is 0—a point to which we shall revert presently; but there is another, and it is at once located between  $\frac{1}{2}$  and 1 with no trouble; and then by trial we find that  $m = 0.554$ , giving  $\lambda = 0.07297/\tau$ , will almost exactly satisfy the equations (8) and (9).

Assuming these values, (7) becomes

$$(H-C)^{-0.554} = 0.07713 + 0.07297t/\lambda, \quad (11)$$

where  $H = 156$ . If by means of this we *calculate* the values of  $C_1$ ,  $C_4$ ,  $C_6$ , we find 125.3, 149.9, 151.6, while the observed values are 130, 149.8, 151;

and these confirm the statement that the first observation was untrustworthy.

Treating the table ( $\beta$ ) in the same way, the equations to be solved are—

$$6^{-m} - 15^{-m} = 2\lambda\tau,$$

$$4^{-m} - 15^{-m} = 3\lambda\tau,$$

which give

$$3(6)^{-m} - 2(4)^{-m} - (15)^{-m},$$

from which we find  $m = 0.184$  and  $\lambda = 0.0558/\tau$ , and therefore

$$(H - C)^{-0.184} = 0.6076 + 0.0558t/\tau, \quad (12)$$

where  $H = 83$ . If from this we calculate the value of  $C_1$ , we find  $C_1 = 73.7$ , while the observed value is 73—a not very different value. This result is to be expected, because with blue light the motion of the spot on the scale is slow enough to allow of an observation at the end of the first 15 seconds.

The curve represented by equation (7), and shown in fig. 4, has an asymptote parallel to OY at a distance  $\{\lambda(H - C_0)^m\}^{-1}$  from OY to the left; and if this asymptote and LM are taken as axes of  $y$  and  $x$  respectively, the equation of the curve is

$$y = \lambda^{-1/m} \cdot x^{-1/m}.$$

For the particular curves (11) and (12), for red and blue, represented in the figure, the distances of the second asymptote from OY are about  $1.6 \times \tau$  and  $10.9 \times \tau$ , respectively.

The importance of a knowledge of the time-current curve is obvious in connection with the measurement of starlight with a selenium bridge, because if we know the nature of the curve, the final value  $H$  of the current due to a star's light can be inferred from two or three observations immediately after exposure, without the necessity for, perhaps, a long delay until the current attains its maximum; in that case the exposure to the light of a given star can be very short. The quantity  $H$  can be found, together with  $m$  and  $\lambda$ , from three equations of the form (7) by making  $t = \tau, 2\tau, 3\tau$  successively.

That a value of  $m$ , distinct from zero, satisfying two equations of the forms (8) and (9) can always be found appears thus—

Suppose that  $H - C_0$  is equal to  $c$ , and that  $H - C$  is  $a$  when  $t = p\tau$ , and  $H - C = b$  when  $t = q\tau$ , where  $p < q$ , and therefore  $a > b$ ; then

$$q(a^{-m} - c^{-m}) - p(b^{-m} - c^{-m}) = 0.$$

Now  $c$  is, of course,  $> a$  and  $> b$ ; and the left side of this equation is

$$q\{(c/a)^m - 1\} - p\{(c/b)^m - 1\},$$

which for some value of  $m$  must vanish, because  $(c/a)^m < (c/b)^m$  for positive

values of  $m$ , so that the multiplier of  $q$  in this expression is less than that of  $p$ , while  $q > p$ , and the ratio of the second coefficient to the first increases indefinitely with  $m$ .

The values of the constants  $m$  and  $\lambda$  depend in some unknown way on the voltage and on the intensity of the light.

When  $H$  is found, the intensity of the light is known from equation (3) into which  $H$  is to be put for  $C$ ,  $i_1$  being the intensity of some standard light which produces a final current  $C_1$ .

### *Effects in the Spectrum.*

Adams and Day found that "the effect was greatest in the greenish yellow and in the red of the solar spectrum, the violet and ultra-red rays producing very little, if any, effect." My observations with a seleno-aluminium bridge are not in complete agreement with this. Passing the light of a Nernst lamp through a quartz lens, in the focus of which the face of the lamp was placed, receiving the parallel emergent beam on a quartz prism, and finally focussing, by means of another quartz lens, the various parts of the spectrum on the end of the long cardboard cylinder employed in these experiments, I examined the effects produced by the rays in, and beyond both extremities of, the spectrum. The end of the cardboard tube on which the spectrum was focussed was closed by a cap in which a slit could be opened; the selenium bridge was placed at the middle of the other end of the tube, 6 metres distant from the slit, and a battery of 2 volts was used. I found a very marked effect produced by rays a long way below the red, and a considerable effect produced by the violet.

The following figure represents roughly the results obtained :

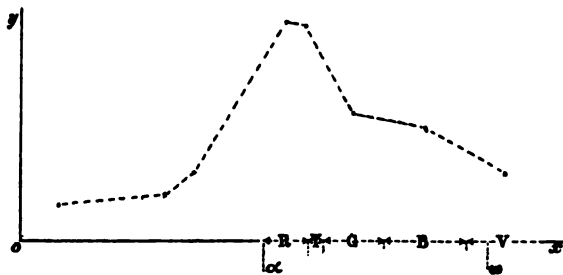


FIG. 5.

The visible spectrum of the lamp is represented in length by  $\alpha\omega$ , and its coloured bands by the letters R, Y, G, B. The yellow Y was a very narrow band, not very well marked, and the violet V was somewhat indefinitely marked beyond the blue.

The ordinates represent the values of  $\delta/R_0$ , where  $R_0$  is the resistance of the bridge in the dark and  $\delta$  the change of resistance produced by the radiation received by the bridge. The maximum is in the red, and it amounted to 0.58. The ordinates corresponding to the angular points of the diagram, counting from 0 towards  $x$ , represent the values

0.09, 0.12, 0.18, 0.58, 0.57, 0.34, 0.30, 0.18.

It appears from this that there is a very considerable effect produced by infra-red radiation.

#### *The Use of Narrow Bridges.*

The purpose for which an almost infinitely narrow bridge of selenium was constructed is to measure the strength of the radiation in various parts of the spectrum of a star by comparing the effect with that of a standard light of the same colour, or the light in the same part of the spectrum of another star.

From the results obtained with red and with blue, it seems that there is little use in exposing a selenium surface to the total light of a star or a planet, as has been hitherto done; for the effects produced by different coloured lights follow different laws as to intensity.

Hence it seems that the most proper course is to use the spectrum of the star, and to expose the selenium to different bands in this spectrum. This I propose to do shortly, on the invitation of Dr. A. A. Rambaut, at the Radcliffe Observatory. The experiments detailed in this paper, made (and still in process) at the Electrical Laboratory, Oxford, were necessary as a preliminary to the stellar work, because it is clearly essential that we should know how to connect the observed effect on the bridge with the intensity of the light producing it, and to ascertain whether the different components of a compound light follow the same law or not. A scarcely less important object is the discovery (even though only approximate) of the nature of the time-current curve.

The experiments of Adams and Day were made with large surfaces of selenium, so that a part of the surface could be exposed to light while the rest was in the dark; and a large part of their work relates to the residual effects (or polarisation currents) produced from the selenium to its electrode when the light is withdrawn. My observation that no such effects are produced in a very narrow seleno-aluminium bridge does not contradict their observations, because the bridge is so narrow that the whole of it must be exposed at once.

Finally, it is necessary to point out the difference between seleno-aluminium *bridges* and the seleno-aluminium *cells* which I used some years

ago. The latter are true "cells," containing a liquid and two metallic surfaces, and they generate a voltage by exposure to light: the former are *resistances* simply; but they will probably prove much more convenient, because they are used with a galvanometer instead of an electrometer.

*On the Theory of Capillarity.*

By E. T. WHITTAKER, Sc.D., F.R.S.

(Received April 29,—Read May 28, 1908.)

§ 1. The fundamental quantities in the theory of capillary phenomena are the *surface-tension*  $\gamma$  (which we shall suppose expressed in dynes per centimetre), and the *surface-energy*  $\lambda$  (which we shall suppose expressed in ergs per square centimetre). The relation between these two quantities is at once given by the thermodynamic equation connecting available energy with total energy: it is therefore

$$\gamma = \lambda + T \frac{d\gamma}{dT}, \quad (1)$$

where  $T$  denotes absolute temperature.

This equation implies that when the area of a surface of separation is increased by 1 cm.<sup>2</sup> at temperature  $T$ , the external agencies do work amounting to  $\gamma$  ergs against the surface-tension: and this energy, together with a further contribution of  $-T d\gamma/dT$  ergs which is appropriated from the heat-energy of neighbouring bodies, becomes resident in the film, giving rise to an increase of  $\lambda$  ergs in its internal energy.

The relation between the surface-tension and surface-energy is, of course, exactly the same as the relation between the electromotive force of a voltaic cell and the energy of the chemical reactions which occur in the cell.

§ 2. As in the comparative theory of chemical substances the heat evolved by a reaction is a more fundamental quantity than the E.M.F. of a cell which can be based on the reaction, so in molecular theory the internal energy of a surface of separation is a more fundamental quantity than the surface-tension to which it gives rise; and it therefore becomes of importance to study the above quantity  $\lambda$ .

Now the value of the surface-tension  $\gamma$  has been experimentally determined for several liquids over wide ranges of temperature by Ramsay and Shields;\* from their results it is possible by the equation (1) above to

\* 'Phil. Trans.,' A, vol. 184, 1893, p. 647.

compute the amount of the surface-energy  $\lambda$ . The writer has done this (see tables below).

One of the peculiarities of the surface-tension observed by Ramsay and Shields, namely the tendency of  $\gamma$  to become insensibly small with rising temperature *before* the critical point is reached, is at once explained when  $\lambda$  is considered: for it appears that, at temperatures approaching the critical point, the term  $-T d\gamma/dT$  is very large compared with the term  $\gamma$  in equation (1), so that in this region the surface-energy consists almost entirely of the term  $-T d\gamma/dT$ , and the surface-tension is (so to speak) a small quantity of the second order. There seems to be no reason for supposing that the surface-energy  $\lambda$  itself vanishes before the critical point is reached.

§ 3. The main object of the writer, however, in computing  $\lambda$  was to see whether it obeyed any simple law or could be represented by any simple formula. This quest has apparently met with success, though it is obvious that an empirical relation based only on the behaviour of five substances over a limited range of temperature, and as yet unsupported by any theoretical explanation, is to be received with caution until further comparison with experimental results is possible.

The relation in question is that *the surface-energy  $\lambda$  of a liquid in contact with its own vapour at any temperature is proportional to the product of the internal latent heat and the (absolute) temperature.*

Perhaps it will be well to define the term "internal latent heat." As is well known, heat supplied for the vaporisation of a liquid is spent in two ways, namely (1) in furnishing the necessary increase of internal energy of the substance as it passes from the state of liquid to that of vapour, and (2) in doing work against external agencies by expansion. The heat expended in the former of these ways is termed the "internal latent heat": by the formula of Clapeyron and Clausius, it is equal to

$$\left(T \frac{dp}{dT} - p\right)(v - v'),$$

where  $p$  denotes the vapour-pressure and  $v'$  and  $v$  the volumes of 1 gramme of the substance before and after vaporisation.

This internal latent heat, which we shall denote by  $\Lambda$ , is intimately connected with Laplace's "intrinsic pressure"  $K$  of a liquid, and so with the classical theory of capillary phenomena.

The empirical formula suggested is, then,

$$\lambda = \text{constant} \times T\Lambda.$$

The characteristic features in the behaviour of  $\lambda$  are as follows. Beginning

with a zero value at (or very near) the critical point,  $\lambda$  at first increases very rapidly as  $T$  decreases; but this rate of increase soon decays, and when the temperature has fallen  $50^\circ$  or  $60^\circ$  below the critical point  $\lambda$  increases much more slowly. A point is at length reached, about  $180^\circ$  below the critical point, at which  $\lambda$  is stationary: and thenceforward  $\lambda$  diminishes as the temperature decreases,—a somewhat surprising result. These changes in  $\lambda$  are identical with the changes of the function  $T\Lambda$ , which has its stationary point at the same temperature as  $\lambda$ .

§ 4. *Tables.*—The following tables illustrate the matter. The five substances considered represent all the non-associating substances investigated by Ramsay and Shields\* for which values of the internal latent heat were immediately available. The tables stop before the neighbourhood of the critical point is reached, but it obviously becomes difficult, as the critical point is approached, to derive trustworthy values of  $\lambda$ , which here consists mainly of the product of the large factor  $T$  into the small and uncertain factor  $d\gamma/dT$ , and is therefore liable to large errors: the values of  $\Lambda$  in this region are probably also very uncertain, and in the present state of experimental knowledge it seems hazardous to carry the comparison of  $\lambda$  and  $T\Lambda$  nearer than  $40^\circ$  or  $50^\circ$  to the critical point; there is, however, a general agreement between  $\lambda$  and  $T\Lambda$  between this point and the critical point, in that they both rapidly decrease to zero.

In the tables, the numbers in the first column are absolute temperatures in Centigrade degrees; in the second column are given the values of the surface-tension  $\gamma$  as found by Ramsay and Shields;† in the third column are the values of  $d\gamma/dT$  derived from these by taking differences and smoothing; in the fourth column, the values of  $\lambda$  derived by equation (1) above from these values of  $\gamma$ ,  $T$ , and  $d\gamma/dT$ ; in the fifth column, values of the internal latent heat  $\Lambda$  in calories, taken from tables given by Mills;‡ and in the last column the values of  $10^4\lambda/T\Lambda$  as calculated from the numbers in the preceding columns.

It will be seen that the numbers in the last column are not strictly constant. They might be made so by altering the estimated values of  $d\gamma/dT$  (from which  $\lambda$  is calculated), without doing great violence to the data; but alterations of this kind are evidently undesirable.

\* *Loc. cit.*† *Loc. cit.*

‡ 'Journ. Phys. Chem.,' vol. 8, p. 383, and vol. 10, p. 1.



## Ethyl Oxide. Critical Temperature, 467°·5 abs.

T.	$\gamma$ .	$\frac{d\gamma}{dT}$ .	$\lambda$ .	$\Lambda$ .	$\frac{10^4\lambda}{T\Lambda}$ .
313	14·05	-0·112	49·1	75·86	20·8
323	12·94	-0·1115	48·9	73·01	20·8
333	11·80	-0·110	48·4	70·79	20·5
343	10·72	-0·108	47·8	68·35	20·4
353	9·67	-0·106	47·1	65·85	20·3
363	8·63	-0·1035	46·1	63·31	20·1
373	7·63	-0·1015	45·5	60·33	20·2
383	6·63	-0·0995	44·7	58·07	20·1
393	5·65	-0·097	43·8	54·91	20·3
403	4·69	-0·094	42·6	51·62	20·5
413	3·77	-0·0905	41·1	48·31	20·6
423	2·88	-0·086	39·3	44·38	20·9

## Methyl Formate. Critical temperature, 487° abs.

T.	$\gamma$ .	$\frac{d\gamma}{dT}$ .	$\lambda$ .	$\Lambda$ .	$\frac{10^4\lambda}{T\Lambda}$ .
308	23·09	-0·153	69·4	107·49	21·3
313	21·56	-0·151	68·8	103·95	21·1
323	20·05	-0·149	68·2	99·51	21·2
333	18·58	-0·147	67·5	95·59	21·2
343	17·55	-0·145	67·3	92·16	21·3
353	15·70	-0·143	66·2	88·03	21·3
363	14·29	-0·141	65·5	85·10	21·2
373	12·90	-0·139	64·6	82·43	21·0
383	11·52	-0·1365	63·8	79·21	21·0
393	10·18	-0·134	62·9	75·92	21·1
403	8·86	-0·1315	61·8	71·95	21·3
413	7·54	-0·128	60·4	68·10	21·5
423	6·30	-0·124	58·8	64·03	21·7

## Carbon Tetrachloride. Critical Temperature, 556° abs.

T.	$\gamma$ .	$\frac{d\gamma}{dT}$ .	$\lambda$ .	$\Lambda$ .	$\frac{10^4\lambda}{T\Lambda}$ .
363	17·60	-0·111	57·9	40·62	39·3
373	16·48	-0·110	57·5	39·68	38·9
383	15·41	-0·108	56·8	38·64	38·4
393	14·32	-0·107	56·4	37·63	38·2
403	13·27	-0·105	55·6	36·58	37·7
413	12·22	-0·103	54·8	35·56	37·3
423	11·21	-0·101	53·9	34·42	37·0
433	10·22	-0·099	53·1	33·28	36·9
443	9·24	-0·096	52·6	32·07	37·0
453	8·28	-0·097	52·2	30·83	37·4
463	7·28	-0·096	51·7	29·52	37·8
473	6·34	-0·094	50·8	28·22	38·1
483	5·40	-0·093	50·3	26·83	38·8
493	4·47	-0·092	49·8	25·35	39·8
503	3·56	-0·087	47·3	23·73	39·6

Benzene. Critical temperature, 561°·5 abs.

T.	$\gamma$ .	$\frac{d\gamma}{dT}$ .	$\lambda$ .	$A$ .	$\frac{10^4 \lambda}{TA}$ .
353	20·28	-0·111	59·5	85·6	19·7
363	19·16	-0·113	60·2	83·7	19·8
373	18·02	-0·115	60·9	82·0	19·9
383	16·86	-0·1155	61·1	80·0	20·0
393	15·71	-0·1145	60·7	78·1	19·8
403	14·57	-0·113	60·1	76·1	19·6
413	13·45	-0·111	59·4	74·1	19·4
423	12·36	-0·110	58·8	71·9	19·3
433	11·29	-0·108	58·0	69·7	19·2
443	10·20	-0·106	57·2	67·5	19·1
453	9·15	-0·104	56·1	65·1	19·0
463	8·16	-0·101	55·0	62·7	19·0
473	7·17	-0·099	54·0	59·9	19·1
483	6·20	-0·097	52·9	57·0	19·3
493	5·25	-0·094	51·5	53·8	19·4
503	4·32	-0·091	49·9	50·5	19·7
513	3·41	-0·087	48·1	46·6	20·1

Chlorobenzene. Critical temperature, 633° abs.

T.	$\gamma$ .	$\frac{d\gamma}{dT}$ .	$\lambda$ .	$A$ .	$\frac{10^4 \lambda}{TA}$ .
423	17·67	-0·0995	59·8	65·81	21·4
433	16·62	-0·10	59·9	64·12	21·6
443	15·67	-0·10	60·0	63·02	21·5
453	14·66	-0·0995	60·0	61·46	21·5
463	13·69	-0·0985	59·8	59·97	21·3
473	12·72	-0·0970	58·6	58·81	21·3
483	11·75	-0·0960	58·1	56·81	21·2
493	10·81	-0·0945	57·4	55·29	21·1
503	9·88	-0·093	56·7	53·83	20·9
513	8·94	-0·0915	55·9	52·43	20·8
523	8·04	-0·09	55·1	50·81	20·7
533	7·14	-0·0875	53·8	49·09	20·6

*On the Aberration of Sloped Lenses and on their Adaptation to Telescopes of Unequal Magnifying Power in Perpendicular Directions.*

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(Received May 20,—Read June 4, 1908.)

The present paper consists of two parts to a large extent independent. The reader who does not care to follow the details of calculation may take the results relative to unsymmetrical aberration for granted. The subject of the second part is somewhat larger than the title. It treats of the advantage which often attends a magnification unequal in different directions and of the methods available for attaining it. Among these is the method of the sloped object-lens. Such sloping introduces in general unsymmetrical aberration. The intention of the first part is largely to show how this may be minimised so as to become unimportant.

PART I.

Before proceeding to actual calculations of the aberrations of a sloped lens, it may be well to consider briefly the general character of a pencil of rays affected with unsymmetrical aberration.

The axis of the pencil being taken as axis of  $z$ , let the equation of the wave-surface, to which all rays are normal, be

$$z = \frac{x^2}{2\rho} + \frac{y^2}{2\rho'} + \alpha x^3 + \beta x^2y + \gamma xy^2 + \delta y^3 + \dots \quad (1)$$

The principal focal lengths, measured from  $z = 0$ , are  $\rho$  and  $\rho'$ . In the case of symmetry about the axis,  $\rho$  and  $\rho'$  are equal, and the coefficients of the terms of the third order vanish. The aberration then depends upon terms of the fourth order in  $x$  and  $y$ , and even these are made to vanish in the formulæ for the object-glasses of telescopes by the selection of suitable curvatures. In the theory of imperfectly constructed spectroscopes and of sloped lenses it is necessary to retain the terms of the third order, but we may assume a plane of symmetry  $y = 0$ , which is then spoken of as the *primary plane*. The equation of the wave-surface thus reduces to

$$z = \frac{x^2}{2\rho} + \frac{y^2}{2\rho'} + \alpha x^3 + \gamma xy^2, \quad (2)$$

terms of higher order being omitted. In (2)  $\rho$  is the primary and  $\rho'$  the secondary focal length.

The equation of the normal at the point  $x, y, z$  is

$$z - \zeta = \frac{\xi - x}{x/\rho + 3\alpha x^2 + \gamma y^2} = \frac{\eta - y}{y/\rho' + 2\gamma xy}, \quad (5)$$

and its intersection with the plane  $\zeta = \rho$  occurs at the point determined approximately by

$$\xi = -\rho(3\alpha x^2 + \gamma y^2), \quad \eta = \frac{\rho' - \rho}{\rho'} y - 2\gamma xy, \quad (6)$$

terms of the third order being omitted.

According to geometrical optics, the thickness of the image of a luminous line (parallel to  $y$ ) at the primary focus is determined by the extreme value of  $\xi$ , and for good definition it is necessary to reduce this thickness as much as possible. To this end it is necessary in general that both  $\alpha$  and  $\gamma$  be small.

We will now examine more closely the character of the image at the primary focus in the case of a pencil originally of circular section. Unless  $\rho' = \rho$ , the second term in the value of  $\eta$  in (6) may be neglected. The rays proceeding from the circle  $x^2 + y^2 = r^2$  intersect the plane  $\zeta = \rho$  in the parabola

$$\frac{\rho\rho'^2(3\alpha - \gamma)}{(\rho' - \rho)^2} \eta^2 - \xi = 3\alpha\rho r^2; \quad (7)$$

and the various parabolas corresponding to different values of  $r$  differ from one another only in being shifted along the axis of  $\xi$ . To find out how much of the parabolic arcs is included, we observe that for any given value of  $r$  the value of  $\eta$  is greatest when  $x = 0$ . Hence the rays starting in the secondary plane give the remainder of the boundary of the image. Its equation, formed from (6) after putting  $x = 0$ , is

$$\eta^2 = -\frac{(\rho' - \rho)^2}{\rho\rho'^2\gamma} \xi, \quad (8)$$

and represents a parabola touching the axis of  $\eta$  at the origin. The whole of the image is included between this parabola and the parabola of form (7) corresponding to the maximum value of  $r$ .

The width of the image when  $\eta = 0$  is  $3\alpha\rho r^2$ , and vanishes when  $\alpha = 0$ , *i.e.*, when there is no aberration for rays in the primary plane. In this case the two parabolic boundaries coincide, and the image is reduced to a linear arc. If, further,  $\gamma = 0$ , this arc becomes *straight*, and then the image of a short luminous line (parallel to  $y$ ) is perfect to this order of approximation at the primary focus. In general, if  $\gamma = 0$ , the parabola (8) reduces to the straight line  $\xi = 0$ ; that is to say, the rays which start in the secondary plane remain in that plane.

We will now consider the image formed at the secondary focus. Putting  $\zeta = \rho'$  in (5), we obtain

$$\xi = \frac{\rho - \rho'}{\rho} x, \quad \eta = -2\gamma\rho'xy. \quad (9)$$

If  $\gamma = 0$ , the secondary focal line is formed without aberration, but not otherwise. In general, the curve traced out by the rays for which  $x^2 + y^2 = r^2$ , is

$$\left(\frac{\rho}{\rho - \rho'}\right)^2 \xi^2 + \frac{(\rho - \rho')^2 \eta}{4\gamma^2 \rho^2 \rho'^2 \xi^2} = r^2 \quad (10)$$

in the form of a figure of 8 symmetrical with respect to both axes. The rays starting either in the primary or in the secondary plane pass through the axis of  $\xi$ , the thickness of the image being due to the rays for which  $x = y = r/\sqrt{2}$ .\*

Or if in order to find the intersection of the ray with the primary plane we put  $\eta = 0$  in (5), we have approximately

$$\xi = \frac{(\rho - \rho')x}{\rho}, \quad \zeta = \frac{1}{1/\rho' + 2\gamma x},$$

showing that  $\zeta$  is constant only when  $\gamma = 0$ .

The calculation of aberration for rays in the primary plane is carried out in the paper cited for the case of a thin lens sloped through a finite angle. If the curvature of the first surface be  $1/r$  and of the second  $1/s$ , and if  $\mu$  be the refractive index, the focal length  $f_1$  in the primary plane is given by

$$\frac{1}{f_1} = \frac{\mu c' - c}{c^2} \left( \frac{1}{r} - \frac{1}{s} \right), \quad (11)$$

and the condition that there shall be no aberration is

$$\frac{(2\mu' + 1)c}{u} + \frac{\mu'^2}{s} + \frac{\mu' - \mu'^2 + 1}{r} = 0. \quad (12)$$

Here  $u$  is the distance of the radiant point from the lens,  $\phi$  the obliquity of the incident ray,  $\phi'$  of the refracted ray,  $c = \cos \phi$ ,  $c' = \cos \phi'$ , and  $\mu' = \mu \cos \phi' / \cos \phi$ .

A result, accordant with (12), but applicable only when  $\phi$  is small, was given in another form by Mr. Dennis Taylor in 'Astron. Soc. Monthly Notices,' Ap., 1893.

If the incident rays be parallel,  $u = \infty$ , and the condition of freedom from aberration is

$$-\frac{r}{s} = \frac{1 + \mu' - \mu'^2}{\mu'^2}. \quad (13)$$

\* The above is taken from my "Investigations in Optics," 'Phil. Mag.,' 1879; 'Scientific Papers,' vol. 1, p. 441, and following. Some errata may be noted:—p. 441, line 9, insert  $y$  as factor in the first term of  $\eta$ ; p. 443, line 9, for (7) read (8), line 10, for  $\eta$  read  $\xi$ .

As appears from (11), opposite signs for  $r$  and  $s$  indicate that both surfaces are convex.

If  $\phi = 0$ ,  $\mu' = \mu$ , so that (13) gives, in this case,

$$-\frac{r}{s} = \frac{1 + \mu - \mu^2}{\mu^2} \dots \quad (14)$$

Thus, if  $\mu = 1.5$ , the aberration vanishes for small obliquities when  $s = -9r$ . This means a double convex lens, the curvature of the hind surface being one-ninth of that of the front surface. If  $s = \infty$ , that is, if the lens be plano-convex with curvature turned towards the parallel rays,

$$1 + \mu - \mu^2 = 0, \quad (15)$$

or

$$\mu = \frac{1}{2}(1 + \sqrt{5}) = 1.618.$$

Returning to finite obliquity, we see from (13) that whatever may be the index and obliquity of the lens, it is possible so to choose its form that the aberration shall vanish. If the form be plano-convex, the condition of no aberration is

$$1 + \mu' - \mu'^2 = 0, \quad (16)$$

or

$$\mu' = \mu \cos \phi' / \cos \phi = 1.618.$$

Here  $\cos \phi' > \cos \phi$ , and the ratio of the two cosines increases with obliquity from unity to infinity. Hence if  $\mu > 1.618$ , there can be no freedom from aberration at any angle. When  $\mu = 1.618$ , the aberration vanishes, as we have seen, when  $\phi = 0$ . If  $\mu$  be less than 1.618, the aberration vanishes at some finite angle. For example, if  $\mu = 1.5$ , this occurs when  $\phi = 29^\circ$ .

In many cases the aberration of rays in the secondary plane is quite as important as that in the primary plane. In my former paper I gave a result applicable to a plano-convex lens, on the curved face of which parallel light falls. It was found that the secondary aberration vanished when the relation between obliquity and refractive index was such that

$$\sin^2 \phi = \frac{3\mu^2 - \mu^4 - 1}{3 - \mu^2}. \quad (17)$$

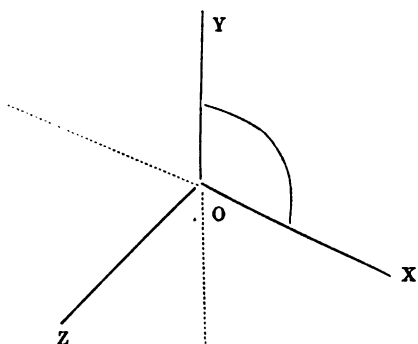
For small values of  $\phi$  this gives the same index as before (15), inasmuch as

$$\mu^4 - 3\mu^2 + 1 = (\mu^2 - 1)^2 - \mu^2 = (\mu^2 - \mu - 1)(\mu^2 + \mu - 1).$$

I inferred that for a plano-convex lens of index 1.618 neither kind of aberration is important at moderate slopes.

Having no note or recollection of the method by which (17) was obtained, and wishing to confirm and extend it, I have lately undertaken a fresh investigation, still limiting myself, however, to *parallel* incident rays. For simplicity, the lens may be supposed to come to a sharp circular edge, the

plane containing this edge being that of  $XY$ . The centre of the circle is the origin, and the axis of  $Z$  is the axis of the lens. The incident rays are parallel



to the plane  $ZX$ , and make an angle  $\Phi$  with  $OZ$ ; so that  $\Phi$  is the angle of incidence for the ray which meets the first surface of the lens at its central point. Everything is symmetrical with respect to the *primary* plane  $y = 0$ . It will suffice to consider the course of the rays which meet the lens close to its edge, of which the equation is  $x^2 + y^2 = R^2$ , if  $2R$  be the diameter.

In order to carry out the calculation conveniently, we require general formulæ connecting the direction-cosines of the refracted ray with those of the incident ray and of the normal to the surface. If we take lengths  $AP$ ,  $AQ$  along the incident and refracted rays proportional to  $\mu$ ,  $\mu'$ , the indices of the medium in which the rays travel, and drop perpendiculars  $PM$ ,  $QN$  upon the normal  $MAN$ , then by the law of refraction the lines  $PM$ ,  $QN$  are equal and parallel; and the projection of  $PA + AM$  on any axis is equal to the projection of  $NA + AQ$  on the same axis. Thus if  $l$ ,  $m$ ,  $n$  are the direction-cosines of the incident ray,  $l'$ ,  $m'$ ,  $n'$  of the refracted ray,  $p$ ,  $q$ ,  $r$  of the normal taken in the direction from the medium in which the light is incident,  $\phi$ ,  $\phi'$  the angles of incidence and refraction,

$$\mu l - \mu \cos \phi \cdot p = -\mu' \cos \phi' \cdot p + \mu' l'$$

and two similar equations. Hence

$$(\mu' l' - \mu l)/p = (\mu' m' - \mu m)/q = (\mu' n' - \mu n)/r = \mu' \cos \phi' - \mu \cos \phi. \quad (18)^*$$

Also

$$\cos \phi = lp + mq + nr, \quad (19)$$

and  $\phi'$  is given by

$$\mu' \sin \phi' = \mu \sin \phi. \quad (20)$$

For our purpose there is no need to retain the two refractive indices, and for brevity we will suppose that the index outside the lens is unity and inside it equal to  $\mu$ ; so that in the above formulæ we are to write  $\mu = 1$ ,  $\mu' = \mu$ . Hence

$$(\mu l' - l)/p = (\mu m' - m)/q = (\mu n' - n)/r = \mu \cos \phi' - \cos \phi. \quad (21)$$

Equation (19) remains as before, while (20) becomes

$$\mu \sin \phi' = \sin \phi. \quad (22)$$

\* See Herman's 'Geometrical Optics,' Cambridge, 1900, p. 22.

For the first refraction at the point  $x, y$ , we have

$$l = \sin \Phi, \quad m = 0, \quad n = \cos \Phi;$$

and if  $\chi_1$  be the angle which the normal to the first surface at the edge of the lens makes with the axis,

$$p = \sin \chi_1 \cdot x/R, \quad q = \sin \chi_1 \cdot y/R, \quad r = \cos \chi_1;$$

so that

$$\frac{\mu l' - \sin \Phi}{x/R \cdot \sin \chi_1} = \frac{\mu m'}{y/R \cdot \sin \chi_1} = \frac{\mu n' - \cos \Phi}{\cos \chi_1} = \mu \cos \phi' - \cos \phi = C_1, \quad (23)$$

$$\text{and} \quad \cos \phi = \sin \Phi \sin \chi_1 \cdot x/R + \cos \Phi \cos \chi_1. \quad (24)$$

In like manner if  $l'', m'', n''$  be the direction-cosines of the twice refracted ray,  $p', q', r'$  those of the second normal, we may take

$$\frac{l'' - \mu l'}{x/R \cdot \sin \chi_2} = \frac{m'' - \mu m'}{y/R \cdot \sin \chi_2} = \frac{n'' - \mu n'}{\cos \chi_2} = \cos \psi' - \mu \cos \psi = C_2, \quad (25)$$

if  $\psi, \psi'$  be respectively the angles of incidence and refraction at the second surface.

$$\text{Here} \quad \cos \psi = l'p' + m'q' + n'r'. \quad (26)$$

Eliminating  $l', m', n'$  between (23) and (25), we get

$$l'' = \sin \Phi + (C_1 \sin \chi_1 + C_2 \sin \chi_2) x/R,$$

$$m'' = (C_1 \sin \chi_1 + C_2 \sin \chi_2) y/R,$$

$$n'' = \cos \Phi + C_1 \cos \chi_1 + C_2 \cos \chi_2.$$

The equation of the ray after passage through the lens is

$$\frac{\xi - x}{l''} = \frac{\eta - y}{m''} = \frac{\zeta}{n''}. \quad (27)$$

The aberration in the secondary plane (depending on  $\gamma$ ) is most simply investigated by inquiring where the ray (27) meets the primary plane  $\eta = 0$ . For the co-ordinates of the point of intersection,

$$\xi = x - \frac{l''y}{m''} = -\frac{R \sin \Phi}{C_1 \sin \chi_1 + C_2 \sin \chi_2}, \quad (28)$$

$$\zeta = -\frac{n''y}{m''} = -R \frac{\cos \Phi + C_1 \cos \chi_1 + C_2 \cos \chi_2}{C_1 \sin \chi_1 + C_2 \sin \chi_2}. \quad (29)$$

In interpreting (28), (29) we must remember that  $\zeta$  is now measured parallel to the axis of the lens and not, as in the preliminary discussion, along the principal ray. Freedom from aberration requires that the line determined by varying  $x$  and  $y$  in (28), (29) should be perpendicular to the principal ray, or that  $\zeta \cos \Phi + \xi \sin \Phi$  should be constant. And

$$-\frac{\zeta \cos \Phi + \xi \sin \Phi}{R} = \frac{1 + (C_1 \cos \chi_1 + C_2 \cos \chi_2) \cos \Phi}{C_1 \sin \chi_1 + C_2 \sin \chi_2}. \quad (30)$$



Before proceeding further it may be well to compare (30) with known results when the aberration is neglected. For a first approximation we may identify  $\phi$  and  $\phi'$  with  $\Phi$  and  $\Phi'$ , and also  $\psi$  and  $\psi'$  with  $\Phi'$  and  $\Phi$  respectively. Thus

$$C_1 = -C_2 = \mu \cos \Phi' - \cos \Phi. \quad (31)$$

Again, if  $r, s$  be the radii of the surfaces, we have, neglecting  $\chi^2$ ,

$$\chi_1 - \chi_2 = R/r - R/s; \quad (32)$$

and thence, from (30),

$$-\frac{1}{\xi \cos \Phi + \xi \sin \Phi} = (\mu \cos \Phi' - \cos \Phi) \left( \frac{1}{r} - \frac{1}{s} \right), \quad (33)$$

the usual formula for the secondary focal length. The reckoning is such that the signs of  $r$  and  $s$  are opposite in the case of a doubly convex lens. We have now to proceed to a second approximation and inquire under what conditions (30) is independent of the particular ray chosen. In the numerator it is sufficient to retain the first power of  $\chi_1, \chi_2$ , so that we may take  $\cos \chi_1, \cos \chi_2$  equal to unity; but in the denominator, which is already a small quantity of the first order, we must retain the terms of the second order in  $\chi_1, \chi_2$ . It is not necessary, however, to distinguish between the sines of  $\chi_1, \chi_2$  and the angles themselves. The first step is to determine corrections to the approximate values of  $C_1$  and  $C_2$  expressed in (31).

For  $\cos \phi$  itself we have, from (24),

$$\cos \phi = \cos \Phi + \chi_1 x/R \cdot \sin \Phi;$$

and again

$$\mu \cos \phi' = \sqrt{\{\mu^2 - 1 + \cos^2 \phi\}} = \mu \cos \Phi' + \frac{\sin \Phi \cos \Phi}{\mu \cos \Phi'} \frac{\chi_1 x}{R},$$

so that 
$$C_1 = (\mu \cos \Phi' - \cos \Phi) \left\{ 1 - \frac{\chi_1 x}{R} \frac{\sin \Phi}{\mu \cos \Phi'} \right\}. \quad (34)$$

In like manner, for  $C_2$  in (26),

$$p' = \chi_2 x/R, \quad q' = \chi_2 y/R, \quad r' = 1,$$

so that

$$\mu \cos \psi = C_1 + \cos \Phi + \sin \Phi \cdot \chi_2 x/R = \mu \cos \Phi' + \frac{x \sin \Phi}{R} \left( \frac{\chi_1 \cos \Phi}{\mu \cos \Phi'} - \chi_1 + \chi_2 \right);$$

and

$$\begin{aligned} \cos \psi' &= \sqrt{\{1 - \mu^2 + \mu^2 \cos^2 \psi\}} \\ &= \cos \Phi + \frac{\mu \cos \Phi' \sin \Phi \cdot x/R}{\cos \Phi} \left( \frac{\chi_1 \cos \Phi}{\mu \cos \Phi'} - \chi_1 + \chi_2 \right); \end{aligned}$$

whence

$$C_2 = (\cos \Phi - \mu \cos \Phi') \left\{ 1 - \frac{x \tan \Phi}{R} \left( \frac{\chi_1 \cos \Phi}{\mu \cos \Phi'} - \chi_1 + \chi_2 \right) \right\}. \quad (35)$$

Thus, if we write  $\mu' = \mu \cos \Phi' / \cos \Phi$ ,

$$C_1 + C_2 = \frac{x \sin \Phi}{R} (\mu' - 1) (\chi_2 - \chi_1); \quad (36)$$

and  $C_1\chi_1 + C_2\chi_2$

$$= \cos \Phi (\mu' - 1)(\chi_1 - \chi_2) + \frac{(\mu' - 1)x \sin \Phi}{\mu' R} \{-\chi_1^2 - (\mu' - 1)\chi_1\chi_2 + \mu'\chi_2^2\},$$
(37)

in which  $\mu'\chi_2^2 - (\mu' - 1)\chi_1\chi_2 - \chi_1^2 = (\chi_2 - \chi_1)(\mu'\chi_2 + \chi_1).$

Accordingly,  $\zeta \cos \Phi + \xi \sin \Phi$

$$= -\frac{R}{(\mu' - 1)\cos \Phi (\chi_1 - \chi_2)} \left\{ 1 + \frac{x \tan \Phi}{\mu' R} [(\chi_2 - \chi_1)(\mu'^2 - \mu') \cos^2 \Phi + \mu'\chi_2 + \chi_1] \right\}$$
(38)

and the condition of no aberration is

$$(\chi_2 - \chi_1)(\mu'^2 - \mu') \cos^2 \Phi + \mu'\chi_2 + \chi_1 = 0. \quad (39)$$

Since  $\chi_1, \chi_2$  are inversely proportional to  $r$  and  $s$ , we may write (39) in the form

$$\frac{1 - (\mu'^2 - \mu') \cos^2 \Phi}{r} + \frac{\mu' + (\mu'^2 - \mu') \cos^2 \Phi}{s} = 0, \quad (40)$$

where  $\mu' = \mu \cos \Phi' / \cos \Phi.$  (41)

If  $s = \infty$ , so that the second surface is flat, we have as the special form of (40)

$$1 - (\mu'^2 - \mu') \cos^2 \Phi = 0; \quad (42)$$

or in the case where  $\Phi = 0$ ,

$$1 + \mu - \mu^2 = 0, \quad (43)$$

the same condition as that (15) required to give zero aberration in the *primary* plane for small obliquities. In the case of finite obliquities we may write (42) in terms of  $\mu$ ,

$$\mu \cos \Phi \cos \Phi' = \mu^2 \cos^2 \Phi' - 1, \quad (44)$$

or if we take the square of both sides of the equation,

$$\mu^2 (1 - \sin^2 \Phi) (1 - \sin^2 \Phi') = (\mu^2 \cos \Phi' - 1)^2.$$

Of this the left-hand side may be equated to

$$(1 - \sin^2 \Phi) (\mu^2 - \sin^2 \Phi) = \mu^2 - (\mu^2 + 1) \sin^2 \Phi + \sin^4 \Phi,$$

while on the right we have

$$(\mu^2 - 1 - \sin^2 \Phi)^2 = (\mu^2 - 1)^2 - 2(\mu^2 - 1) \sin^2 \Phi + \sin^4 \Phi;$$

so that

$$\sin^2 \Phi = \frac{3\mu^2 - \mu^4 - 1}{3 - \mu^2}, \quad (45)$$

as formerly found (see (17)).

In interpreting (45), which we may also write in the form

$$\sin^2 \Phi = \frac{(\mu^2 - \mu - 1)(\mu^2 + \mu - 1)}{\mu^2 - 3}, \quad (46)$$

we must bear in mind that it covers not only the necessary equation (44), but also the equation derived from (44) by changing the sign of one of the members. For instance, if we put  $\mu = 1$  in (46), we derive  $\sin^2 \Phi = \frac{1}{2}$ , or  $\Phi = 45^\circ$ ; but on referring back we see that these values satisfy, not (44), but

$$-\mu \cos \Phi \cos \Phi' = \mu^2 \cos^2 \Phi' - 1.$$

The transition occurs when  $\cos \Phi = 0$ , or  $\Phi = 90^\circ$ , when (45) gives  $\mu^2 = 2$ , or  $\mu = 1.4142$ . For smaller values of  $\mu$  there is no solution of (44). Onwards from this point, as  $\mu$  increases,  $\Phi$  diminishes. For example, when  $\mu = 1.5$ ,  $\sin^2 \Phi = \frac{1}{2}$ , whence  $\Phi = 73^\circ$ . The diminution of  $\Phi$  continues until  $\mu^2 - \mu - 1 = 0$ , or  $\mu = 1.618$ , when  $\Phi = 0$ , so that this is the value suitable for a plano-convex lens at small obliquities. After this value of  $\mu$  is exceeded,  $\sin^2 \Phi$  in (46) is negative until  $\mu^2 = 3$ , or  $\mu = 1.732$ . When this point is passed,  $\sin^2 \Phi$  becomes positive, but a real value of  $\Phi$  is not again reached. We infer that in the case of a plano-convex lens (curved face presented to parallel rays) there can be no freedom from secondary aberration unless  $\mu$  lies between the rather narrow limits 1.414 and 1.618.

If the plano-convex lens be so turned as to present its plane face to the parallel rays,  $r = \infty$ ; and (40) requires that

$$\mu' + (\mu'^2 - \mu') \cos^2 \Phi = 0,$$

which cannot be satisfied, since  $\mu' > 1$ .

Leaving now the particular case of the plano-convex lens, let us suppose in the general formula (40) that  $\Phi = 0$ . We have

$$\frac{1 + \mu - \mu^2}{r} + \frac{\mu^2}{s} = 0, \quad (47)$$

from which we see that, whatever may be the value of  $\mu$ , compensation may be attained by a suitable choice of the ratio  $r:s$ . If  $\mu < 1.618$ ,  $r$  and  $s$  have opposite signs, that is, the lens is double convex; while if  $\mu > 1.618$ ,  $r$  and  $s$  have the same sign, or the lens is of the meniscus form. For example, if  $\mu = 1.5$ , (47) gives  $s = -9r$ , so that the lens is double convex, the hind surface having one-ninth the curvature of the front surface.

We have seen that the aberrations in both the primary and the secondary planes are eliminated for small obliquities in the case of a plano-convex lens if  $\mu = 1.618$ . The question arises whether this double elimination is possible at finite obliquities if we leave both the form of the lens and the refractive index arbitrary. It appears that this can *not* be done. The necessary condition is by (13), (40)

$$-\frac{s}{r} = \frac{\mu'^2}{1 + \mu' - \mu'^2} = \frac{\mu' + (\mu'^2 - \mu') \cos^2 \Phi}{1 - (\mu'^2 - \mu') \cos^2 \Phi},$$

or

$$\frac{\mu'}{1 + \mu' - \mu'^2} = \frac{\mu' - (\mu' - 1) \sin^2 \Phi}{1 + \mu' - \mu'^2 + (\mu'^2 - \mu') \sin^2 \Phi},$$

whence  $(\mu'^2 - 1) \sin^2 \Phi = 0,$  (48)

which can be satisfied only by  $\Phi = 0$ , since  $\mu' > 1$ .

Since it is not possible to destroy both the primary and secondary aberrations when the angle of incidence is finite, it only remains to consider a little further in detail one or two special cases.

We have already spoken of the plano-convex lens; but for a more detailed calculation it may be well to form the equation for absence of primary aberration analogous to (45). From (16),

$$\mu \cos \phi' \cos \phi = \mu^2 - 1, \quad (49)$$

whence, if we square both sides,

$$\sin^4 \phi - (\mu^2 + 1) \sin^2 \phi + 3\mu^2 - \mu^4 - 1 = 0,$$

giving  $\sin^2 \phi = \frac{\mu^2 + 1 \pm \sqrt{5}(\mu^2 - 1)}{2},$  (50)

so that  $\sin^2 \phi = 1.618034 - 0.618034 \mu^2,$  (51)

the other root being excluded if  $\mu > 1$ . It may be remarked that there is no distinction between  $\phi$  here and  $\Phi$  in (45).

The following table will give an idea of the values of  $\phi$  from (51) and (45) for which the plano-convex lens of variable index is free from aberration in the primary and secondary planes respectively.

$\mu$ .	$\phi$ . Primary plane.	$\phi$ . Secondary plane.
	° ' ,	° ' ,
1.0000	90 0	—
1.4142	38 11	90 0
1.5000	28 29	73 13
1.5500	21 24	58 37
1.5900	13 38	39 45
1.6000	10 55	32 25
1.6100	7 16	22 1
1.6180	0 0	0 0

In the above the curved face is supposed to be presented to the parallel rays. If the lens be turned the other way,  $r = \infty$ , and (13) gives  $\mu' = 0$ , an equation which cannot be satisfied. In this case neither the primary nor the secondary aberration can be destroyed at any angle.

Next suppose that the lens is equi-convex, so that  $s = -r$ . In this case (13) gives

$$\mu'^2 - \frac{1}{2}\mu' - \frac{1}{2} = 0, \quad (52)$$

whence  $\mu' = 1$ , or  $-\frac{1}{2}$ , of which the latter has no significance. Also from (40) we get  $\mu' = 1$ . It appears that neither aberration can vanish for an equi-convex lens, unless in the extreme case  $\mu = 1$ ,  $\phi = 0$ , when the lens produces no effect at all.

## PART II.

It is a common experience in optical work to find the illumination deficient when an otherwise desirable magnification is introduced. Sometimes there is no remedy except to augment the intensity of the original source of light, if this be possible. But in other cases the defect may largely depend upon the manner in which the magnification is effected. With the usual arrangements magnifying takes place equally in the two perpendicular directions, though perhaps it may only be required in one direction. For example, in observations upon the spectrum, or upon interference bands, there is often no need to magnify much, or perhaps at all, in the direction parallel to the lines or bands. If, nevertheless, we magnify equally in both directions, there may be an unnecessary and often very serious loss of light.

In discussing this matter there is another distinction to be borne in mind. Sometimes it is not necessary or advantageous that there should exist a point-to-point correspondence between the object and the image. It suffices that a point in the object be represented in the image by a narrow line. This happens, for example, in the use of Rowland's concave gratings. A conspicuous instance occurs in the refractometer which I described in connection with observations upon argon and helium.\* Here while the object-glass of the telescope was as usual, a very high magnification in one direction was secured by the use, as sole eye-piece, of a cylindrical lens taking the form of a glass rod 4 mm. in diameter. An equal magnification in both directions, such as would have been afforded by the usual spherical eye-pieces, would have so reduced the light as to make the observations impossible.

Whenever the field of view varies only in one dimension, there is usually no loss, and there may even be gain in the presence of astigmatism. In other cases a point-to-point correspondence between image and object is desirable or necessary, and the question arises how it may best be attained otherwise than by the use of a common telescope, which limits the mag-

\* 'Roy. Soc. Proc.' vol. 59, p. 198, 1896; 'Scientific Papers,' vol. 4, pp. 218, 364.

nification in the two directions to equality. I had occasion to consider this problem in connection with observations upon Haidinger's rings as observed with a Fabry and Perot apparatus. Here the field is symmetrical about an axis, and all the advantage that magnification can give is secured though it take place only in one direction. At the same time light is usually saved by abstaining from magnifying in the second direction also. In this way the circular rings assume an elongated elliptical form—a transformation which in no way prejudices observation by simple inspection. The question whether light is saved, as compared with symmetrical magnification, depends of course upon the aperture available in the two directions. In a Fabry and Perot apparatus this is usually somewhat restricted.

One simple solution of the problem, available when the light is homogeneous, may be found in the use of a *magnifying prism*, that is a prism so held that the emergence is more nearly grazing than the incidence. In this way we may obtain a moderate magnification in one direction combined with none at all in the second direction. A magnification equal in both directions may then be superposed with the aid of a common telescope. This method would probably answer well in certain cases, but it has its limitations. Moreover, the accompanying deviation of the rays through a large angle would often be inconvenient.

If we are allowed the use of cylindrical lenses, or of lenses whose curvature though finite is different in the two planes, we may attain our object with a construction analogous to that of a common telescope. Suppose that the eye-piece is constituted of a spherical and a contiguous cylindrical convex lens. In one plane the power of the eye-piece is greater than in the other perpendicular plane. Thus, if the object-glass be composed of spherical lenses only, there cannot be complete focussing. With the spherical lens or lenses of the object-glass, mounted as usual, it is necessary to combine a cylindrical lens of comparatively feeble power, which may be either convex or concave. All that is necessary to constitute a telescope in the full sense of the word, that is an apparatus capable of converting incident parallel rays into emergent parallel rays, is that the usual condition connecting the focal lengths of object-glass and eye-piece should be satisfied for the two principal planes taken separately. The magnifying powers in the two planes may thus be chosen at pleasure; and since there is symmetry with respect to both planes the apparatus is free from the unsymmetrical aberration expressed in (1).

When the magnifying desired is considerable in both planes, there is but little for the cylindrical component of the object-glass to do, and it occurred to me that it might be dispensed with, provided a moderate slope were given

to the single (spherical) lens. In the earlier experiments the object-glass was a nearly equi-convex lens of 14 inches focus. The eye-piece was a combination of a spherical lens of 6 inches focus with a cylindrical lens of  $2\frac{1}{2}$  inches focus, so that the focal lengths of the combination were about 2 inches and 6 inches in the principal planes, giving a *ratio* of magnifications as three to one. With the above object-lens the actual magnifications would be about 2 and 6. During the observations the axis of the telescope was horizontal and that of the cylindrical lens vertical, so that the higher magnification was in the horizontal direction of the field. During the adjustments it is convenient to examine a cross formed by horizontal and vertical lines, ruled upon paper well illuminated and placed at a sufficient distance.

When the object-lens stands square, there is, of course, no position of the compound eye-piece which allows both constituents of the cross to be seen in focus together. If we wish to pass from the focus for the horizontal to that necessary for the vertical line, we must push the eye-piece in. In order to focus both at once we must slope the object-lens. And since while both the primary and secondary focal lengths are diminished by obliquity the former is the *more* diminished, it follows that the sloping required is in the vertical plane, the lens being rotated about its horizontal diameter. If we introduce obliquity by stages, we find that the displacement of the eye-piece required to pass from one focus to the other gradually diminishes until an obliquity is reached which allows both lines of the cross to be in focus simultaneously. At a still higher obliquity the relative situation of the two foci is reversed. In the actual experiment with the 14-inch object-lens, the critical obliquity was roughly estimated at about  $30^\circ$ .

The above apparatus worked fairly well when tried upon interference rings from a thallium vacuum tube. But it was evident that the image suffered somewhat from aberration. A better result ensued when the magnification in both directions was increased by the substitution of an object-lens of 24 inches focus, although this also was equi-convex.

Being desirous of testing the method of the sloped lens under more favourable conditions, I procured from Messrs. Watson a lens of baryta crown glass of index for mean rays 1.59, and of *plano-convex* form. The aperture was about  $1\frac{1}{2}$  inch, and the focal length 24 inches. When this was combined with the compound eye-piece already described, the performance was very good, if, in accordance with the indications of theory, the curved face of the object-lens was presented to the incident light. The test may be made either upon a cross or upon a system of concentric circles drawn upon paper. The angle of slope giving the best effect was now very sharply

defined. When, however, the object-lens was reversed, so as to present its plane face to the incident rays, no good result could be attained, evidently in consequence of aberration. The change in the character of the image was now very apparent when the eye was moved up and down, the rings appearing more elliptical as the eye moved in the direction of the nearest part of the edge of the sloped lens. Next to nothing of this effect could be observed when the object-lens was used in the proper position. It is scarcely necessary to say that care must be taken to ensure that the axis, about which the lens is turned, is truly perpendicular to the axis of the cylindrical component of the eye-piece.

Altogether it appears that the combination of sloped object-lens with compound cylindrical eye-piece constitutes a satisfactory solution of the problem. I believe that it may be applied with advantage in the many cases which arise in the laboratory where an unsymmetrical magnifying best meets the conditions. The question as to the precise index to be chosen for the plano-convex lens remains to some extent open. Possibly a somewhat higher index, *e.g.*, 1.60, or even 1.61, might be preferred to that which I have used.

With the view to the design of future instruments, it may be convenient to set out the formula giving the distance between the primary and secondary foci of the object-lens as dependent upon the obliquity  $\phi$ . If  $f_1, f_2$  be the primary and secondary focal lengths, it is known (compare (33)) that

$$\frac{f_0}{f_1} = \frac{\mu \cos \phi' - \cos \phi}{(\mu - 1) \cos^2 \phi}, \quad (53)$$

$$\frac{f_0}{f_2} = \frac{\mu \cos \phi' - \cos \phi}{\mu - 1}, \quad (54)$$

$f_0$  being the focal length corresponding to  $\phi = 0$ ; so that

$$\frac{f_2 - f_1}{f_0} = \frac{(\mu - 1) \sin^2 \phi}{\mu \cos \phi' - \cos \phi}. \quad (55)$$

In this

$$\mu \cos \phi' - \cos \phi = \sqrt{(\mu^2 - \sin^2 \phi)} - \sqrt{(1 - \sin^2 \phi)} = (\mu - 1) \left\{ 1 + \frac{\sin^2 \phi}{2\mu} \right\}$$

approximately. Hence

$$\frac{f_2 - f_1}{f_0} = \sin^2 \phi \left\{ 1 - \frac{\sin^2 \phi}{2\mu} \right\}, \quad (56)$$

from which the required obliquity is readily calculated when the nature of the eye-piece and the focal length of the object-lens are given.

P.S., June 6.—From von Rohr's excellent 'Theorie und Geschichte des Photographischen Objectivs,' Berlin, 1899, I learn that Rudolf and, at a still



earlier date (1884), Lippich had proposed a different method of obtaining a diverse magnification, and one that I had overlooked. This consists in the use of an eye-piece formed by crossing two cylindrical lenses of different powers. The two lenses are mounted, not close together, but at such distances from the image as to render parallel the rays diverging from it in the two planes separately. In this method the object-lens remains square to the axis of the instrument. Lippich had the same object in view as that which guided me. I have tried his method with success, obtaining an image as good, or nearly as good, as that afforded by the sloped lens. I understand that Professor S. P. Thompson also has used a similar device.

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*The Optical Constants of Gypsum at different Temperatures, and the Mitscherlich Experiment.*

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At a lecture delivered to the Prussian Academy of Sciences in the year 1826, Professor Mitscherlich showed an optical experiment with gypsum (selenite) which has ever since been known as the "Mitscherlich experiment." He had discovered, as the most striking result of an investigation of the double refraction of a number of crystallised substances at varying temperatures, that gypsum, the crystallised hydrated sulphate of lime,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , suffers greater change, as regards the position of its optic axes, under the influence of heat than any other substance then examined. At the ordinary temperature it is biaxial, with an optic axial angle of about  $60^\circ$ , but on raising the temperature the angle diminishes until in the neighbourhood of the temperature of boiling water the axes come together, producing in convergent polarised light the rectangular cross and circular rings of a uniaxial crystal. Beyond that temperature the axes again separate, but in the direction at right angles to their former one. On allowing the crystal section-plate to cool, the phenomena are repeated in the reverse order. It was this striking experiment which was shown for the first time by Mitscherlich in the lecture in Berlin above referred to.

The experiment is one that is often now repeated, as one of the most interesting and easily demonstrated cases of "crossed-axial-plane dispersion." Other well-known cases are brookite, the rhombic form of titanium dioxide

TiO<sub>2</sub>, and the triple tartrate of potassium, sodium, and ammonium. But these two other cases differ from that of gypsum, inasmuch as the crossing of the optic axial planes occurs at the ordinary temperature by varying the wave-length of the light employed from one end of the spectrum to the other, the axes being separated in one plane for the red end and in the perpendicular plane for the blue end, while for light of a specific intermediate wave-length the uniaxial figure is produced. The crossing in the case of gypsum, however, is brought about by changing the temperature, change of wave-length producing but little effect at the ordinary temperature, the interference figure being one that shows but slight dispersion, the difference of optic axial angle for red and for blue being only about a couple of degrees.

The usual mode of showing the Mitscherlich experiment on the screen, with the aid of the lantern projection polariscope, is to place a somewhat large section-plate of gypsum, cut perpendicular to the acute bisectrix of the optic axial angle, in a metal frame having a projecting part which can be heated by a spirit lamp or small Bunsen flame. A strip of sheet brass with a hole cut in the middle large enough to admit the crystal plate, and bent away from the object-stage near each end, so as to enable it to be heated without injuring the latter, serves very well. The crystal plate may be maintained in position by bending a thin card round both sides of the middle portion of the strip, a pair of apertures slightly smaller than the crystal, cut out of the card at opposite positions, serving as a diaphragm, to allow only the light from the central portion of the crystal to pass to the screen.

But it may be performed more simply and elegantly, and without sacrificing any light, by making the plate very small, about 6 mm. square, while still of adequate thickness (2 mm.) to ensure a sharp interference figure. There is no necessity for the plate to be much larger than the focal spot of light from the converging system of lenses, but some thickness is desirable on account of the very low double refraction. With such a small plate—held in a little platinum-foil or thin brass carrier-frame\* barely larger than the plate (7 by 6 by 3 mm.), with an aperture just larger (3 mm.) than the focal spot, and provided with a little lip to enable it to be gripped by a miniature hard-wood holder to avoid conduction away of heat, which is gripped in turn by the ordinary metallic crystal holder—the experiment may be caused to proceed beautifully *regularly by the heat of the rays from the lantern alone.* Moreover, a water

\* Small plates of selenite thus mounted are prepared by the firm of Steeg and Reuter, and may be obtained from Messrs. Newton.

or alum cell may, and should still, be employed between the lantern condenser and the large Nicol-prism polariscope, in order to save injury to the balsam film of the prisms. If the convergent and redivergent lens-systems have been properly adjusted, so that their common focus is in the centre of the little crystal section, the moment the electric arc of the lantern is switched on the coloured rings surrounding the two optic axes, just visible on the screen at the right and left margins of the field, begin to move towards the centre, the axial hyperbolic dark brushes themselves soon appear and continue to march steadily towards the centre at an accelerating rate, while the surrounding rings and lemniscates exhibit an ever changing and more and more brilliant display of spectrum colours in succession, until the brushes coalesce in the centre itself to form the uniaxial rectangular cross, the surrounding spectrum curves becoming concentric circles. Quite as steadily the cross again opens out, as the temperature still rises, into hyperbolic brushes separating more and more in the vertical direction of the field, that is, at right angles to their former line of separation. As soon as they are well separated in this plane, the crystal can be saved from becoming incinerated to plaster of Paris (gypsum losing its water of crystallisation at  $120^{\circ}$  C.) by interposing an opaque object such as a cardboard or metal disc between the lantern and the polariscope. By successively introducing and removing this disc matters can be so arranged that the temperature becomes slowly lowered, and the reverse phenomena of repassing the crossing stage and rediverging in the horizontal plane observed. Indeed, by suitable manipulation of the disc the axes may be made to move on the screen either way to or from the crossing point, and retained about the latter for any length of time.

(The experiment as thus described was demonstrated to the Society, with the aid of a fine Nicol-prism projection polariscope recently constructed for the author by Messrs. Harvey and Peak for crystallographic demonstrations. The two Nicols are a perfect pair of Iceland-spar prisms of over 2 inches minimum aperture, made by Mr. Ahrens, and are carried in rotatable mounts provided with silvered divided circles, and closed at one end with parallel glass, a cell screwing into the other end, which may carry either a concave parallelising lens, a parallel-glass plate, or a ground-glass plate for use in table illumination. The Nicols thus mounted are supported in each case by two columns, adjustable for height, rising from a basal slider. The various lenses, crystal holders and stages, signal-slits, the optic-axial-angle goniometer, and other accessories, are all separately mounted on columns similarly adjustable for height, and also for rotation and transverse position, carried on similar sliders, as narrow in the axial direction of the whole optical

arrangement as is compatible with stability, and provided with fixing screws. The whole of the sliders are capable of sliding in a correspondingly grooved base-bed, 32 inches long, and of being arranged, re-arranged, and interchanged at the experimenter's will, no tubes or other limitations being in the way of either compact or open order. The arrangement of the parts used for the Mitscherlich experiment was as follows :—(1) A water cell, 2 inches thick, immediately after the lantern condenser delivering a slightly converging beam ; (2) the polarising Nicol rotated  $45^\circ$  to right ; (3) a plano-convex lens of 5 inches focus and  $2\frac{1}{4}$  inches diameter ; (4) the optic-axial-angle goniometer, consisting of the convergent system of three lenses, the crystal carried by a goniometrically mounted holder, and the redivergent system of three lenses, all carried by a single pedestal, the two equal and opposite lens systems having adjustments for closeness to crystal ; (5) a doubly convex field lens ; (6) the achromatic projection lens ; and (7) the analysing Nicol rotated  $45^\circ$  to left.)

The phenomenon of crossed-axial-plane dispersion is not one which is very frequently exhibited by crystals, but it has been the author's good fortune to meet with no less than six cases during his investigations, namely, rubidium sulphate, caesium selenate, ammonium selenate, caesium magnesium sulphate, and the selenate of the same two metals, and also an organic substance, the monoclinic form of ethyl triphenyl pyrrolone. In a communication to the '*Zeitschrift für Krystallographie*,'\* the phenomena exhibited were compared, and a general explanation arrived at. In all this work, the spectroscopic monochromatic illuminator described to the Royal Society by the author in 1895† has proved of inestimable value, enabling the precise wave-length corresponding to the production of the uniaxial figure to be determined in every case.

The requisite conditions for crossed-axial-plane dispersion were shown to be the following :—

(1) *The simultaneous occurrence of extremely small double refraction (nearness of the  $\alpha$ - and  $\gamma$ -indices of refraction), and close approximation of the intermediate index  $\beta$ , either to the  $\alpha$ - or to the  $\gamma$ -index.* The latter condition is necessary for the possibility of crossing, and the former for wide separation of the optic axes in the two planes for the two ends of the spectrum, or for two different temperatures.

(2) *Change of wave-length of the light employed at the ordinary temperature, or change of temperature, while using light of the same wave-length, or both kinds of change simultaneously operating, must so act as to bring about equality, at a*

\* 1906, vol. 42, p. 554.

† '*Phil. Trans.*' A, vol. 185, p. 913.

*particular temperature for each wave-length, of two of the three axes of the optical ellipsoid (either the indicatrix or the Fresnel ellipsoid), namely, the intermediate axis and that one of the other two which is already nearest to equality to it. As the axes of the indicatrix are directly, and those of the Fresnel ellipsoid inversely, proportional to the indices of refraction along the three rectangular directions corresponding to the principal axes of the ellipsoid, this means that the uniaxial cross is produced, owing to two of the three refractive indices becoming equal at the particular temperature, and for the specific wave-length in question.*

The extreme delicacy of the situation when condition (1) is fulfilled will be appreciated when it is remembered that the dispersion for different wave-lengths of light is different for each of the three refractive indices, and that the effect of change of temperature is also different along the three axial directions of the ellipsoid, thus further disturbing the balance. As a change of only a few units in the fourth decimal place of the refractive index may be adequate, when all three indices are so close together as they are in these cases to start with, to provoke complete reversal of the relative positions of two of the three indices, it is readily conceivable that these directional slight differences of dispersion may suffice to bring about the changes demanded by condition (2).

The two classes of crystals showing crossed-axial-plane dispersion which have been referred to, namely, those particularly sensitive to change of temperature and those more sensitive to change of wave-length, pass into each other so gradually that no line of demarcation can be drawn. The five sulphates and selenates, exhaustively studied, proved to be more or less intermediate cases sensitive to both, and, in the case of caesium selenate, a very stable substance which can be safely heated to  $250^{\circ}$ , the changes are so rapid that each of the three axes of the optical ellipsoid in turn becomes the first median line. But gypsum is pre-eminently characteristic of those most affected by variation of temperature, although, owing to its low decomposition temperature, the phenomena cannot be followed beyond  $120^{\circ}$ ; while brookite and the triple tartrate of the alkalies are excellent examples of those extremely sensitive to change in the colour of the light. Thus, while gypsum requires the plate perpendicular to the first median line to be warmed to over  $100^{\circ}$  in order to bring about the formation of the uniaxial figure, brookite and triple tartrate show it at the ordinary temperature by illuminating the polariscope with light of all the colours of the spectrum in succession. When this is done by means of the spectroscopic monochromatic illuminator, which supplies monochromatic light of the order of purity of the two-hundredth part of the visible spectrum, and at the same time records the wave-length,

a wave-length curve corresponding to the divisions of the circle carrying the prism, it is easy to stop when the uniaxial figure is exactly formed, and to read off the circle division, and thence, with the aid of the curve, the wave-length corresponding.

The refractive indices of gypsum appear never to have been determined for temperatures higher than the ordinary, so that it has hitherto been impossible to verify the author's general explanation of crossed-axial-plane dispersion in this very important case. It was suggested, however, in the memoir already quoted, that the theory would be found to be equally applicable to gypsum, and the work now described was instituted with the object of definitely settling the question. Moreover, during the investigation of the six cases already mentioned as having been studied, it was observed that different crystals of any one of them often showed considerable differences of optic axial angle for the same temperature and wave-length, due to the delicate balance of the three indices, and to the fact that the very minute differences of refraction shown by crystals from different crops of the same substance, owing to corresponding minute differences in the circumstances of growth, are capable in these sensitive cases of provoking quite considerable changes of optic axial angle. It will therefore be obvious, that if the usual method of determining the optical constants is followed, of cutting one prism from one crystal to afford  $\alpha$  and  $\beta$ , and a second prism from another crystal to afford  $\beta$  and  $\gamma$ , and also two section-plates perpendicular respectively to the first and second median lines from two different crystals, the constants arrived at by the combination of the experimental results thus derived from four different crystals may be very inaccurate, and, at any rate, cannot be put forward with full confidence. Clearly, the only trustworthy procedure is to cut both prisms and both plates from one and the same crystal, when we shall be sure that the results for the refractive indices and for the true angle between the optic axes are correct for that particular crystal, which should be selected on account of its crystallographic perfection, absolute transparency, and freedom from impurity.

This is precisely what has been done in the case of this investigation of gypsum.

The crystal selected was a particularly clear and transparent one from Wiesloch (Baden), supplied by Mr. Butler. It is represented in fig. 1. It will be remembered that gypsum (selenite) crystallises in the monoclinic system, and in the holohedral (prismatic) class of that system. The single symmetry plane is the plane of the perfect cleavage of the mineral, which enables thin plates of selenite to be prepared with the greatest ease for the numerous polariscopical purposes for which selenite is so famous. The same

plane, however, contains the two median lines, being the plane of the optic axes, and the very excellence of the cleavage offers the greatest difficulty to the preparation of the section-plates, for they obviously have to be cut across the cleavage. The difficulty has been successfully overcome, however, and the author desires to record his thanks to Mr. Twyman, of the firm of Hilger, for the great care taken both to avoid cleavage fracture and to render the polished surfaces truly plane and accurately orientated. The reflections afforded by the whole of the eight surfaces are optically perfect and sharp.

The crystal was not rich in faces; besides the clinopinacoid  $b(010)$ , parallel to the symmetry plane and, as is usual with selenite, the form most prominently developed (the crystal being tabular thereon although thick), there were only present the two forms,  $p(110)$ , the monoclinic primary prism, and  $o(111)$ , the primary hemi-pyramid. The stereographic pro-

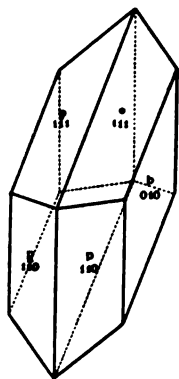


FIG. 1.

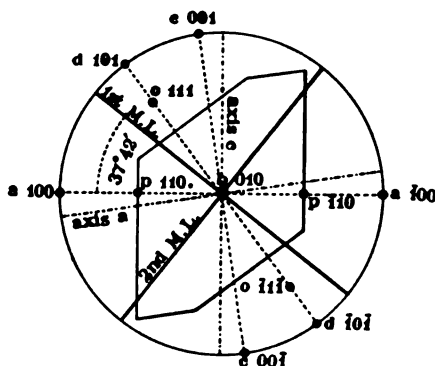


FIG. 2.

jection showing the poles of these forms is given in fig. 2, and on it are also shown the poles of three other forms. One is the orthopinacoid  $a(100)$ , which is sometimes developed but was not present on the crystal in question, and which if present replaces the edge  $pp = 110:1\bar{1}0$ ; another is the other crystallographic axial-plane form  $c(001)$ , the basal pinacoid, and the third is the ortho-prism  $d(101)$  which replaces the edge  $oo = 111:1\bar{1}1$ . An outline of the crystal is also shown in the figure, representing the section of the crystal by the symmetry plane, assuming the forms  $a$ ,  $d$ , and  $c$  to be all present the better to indicate the symmetry. The actual crystal would give the same section, except that the top and bottom corners would not be cut off by the basal pinacoid, which is not present. These crystallographic data in the drawing will help to make quite clear the positions of the crystallographic axes  $a$  and  $c$  ( $b$  being perpendicular to the paper), which are marked in dotted-and-broken lines, and of the normals to the faces  $a$ ,  $d$ , and

$c$ , which are drawn in broken lines. The positions of the optical first and second median lines are also shown in strong continuous lines; these are the two extreme axes of the optical ellipsoid, the intermediate axis being perpendicular to the paper.

The crystal was 13.5 mm. in thickness, and 48 and 27 mm. respectively along the diagonals (measured parallel to the tabular clinopinacoid, the symmetry plane).

Fig. 3 shows the scheme according to which the crystal was cut, assuming it to be lying on a clinopinacoid face. The triangular end-part A was used for the stauroscopic determinations of the directions of extinction (the directions of the first and second median lines, the extreme axes of the ellipsoid and the bisectrices of the acute and obtuse optic axial angles). Similar determinations with sodium light had previously been carried out with the whole crystal, in order to be certain of the precise directions of the axes of the ellipsoid before commencing the cutting. B was the plate perpendicular to the first median line. C was the  $60^\circ$  prism affording  $\beta$  and  $\gamma$ . The refracting edge is represented in plan by the apex, the edge itself being parallel to the symmetry axis (perpendicular to plane of paper); the bisecting plane contains that axis, which is the intermediate axis of the ellipsoid (corresponding to the index  $\beta$ ), and the first median line, the latter being the minimum axis of the Fresnel ellipsoid and maximum axis of the indicatrix, corresponding to the  $\gamma$ -index. D was a piece left in reserve in case of accidental fracture along a cleavage direction during cutting. E was

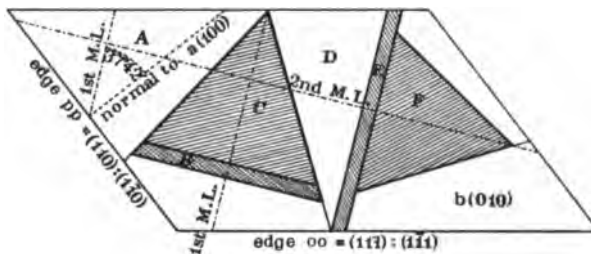


FIG. 3.

the section-plate perpendicular to the second median line. Finally, F was the  $60^\circ$  prism affording  $\alpha$  and  $\beta$ . Its refracting edge indicated by the apex in the drawing is also parallel to the symmetry axis  $b$  like that of C, and thus this prism also affords  $\beta$ , which is consequently obtained in duplicate, once from each prism, and the concordance of these values will afford an excellent criterion of the accuracy of the work. Its bisecting plane contains, besides this axis  $\beta$  of the ellipsoid, the second median line, the



maximum axis of the Fresnel ellipsoid or minimum axis of the indicatrix, so that this second direction of vibration of the light passing through the prism at minimum deviation corresponds to the  $\alpha$ -index. It will thus be clear that each of the two prisms afforded, when arranged for minimum deviation, two images of the signal slit of the refractometer; one corresponded to light vibrating parallel to the refracting edge (in both cases the intermediate axis of either ellipsoid and corresponding to the  $\beta$ -index), and extinguishing when the Nicol was at  $0^\circ$ , and the other to light vibrating parallel to one of the two median lines (the minimum or maximum axis of the ellipsoid corresponding to  $\alpha$  in one case and  $\gamma$  in the other), and extinguishing when the Nicol was at  $90^\circ$ . This is the first time that the indices, even for the ordinary temperature, have been thus all three directly determined, for the determinations of von Lang were made with a single prism yielding only  $\beta$  directly,  $\alpha$  and  $\gamma$  being obtained by an indirect method.\* The degree of accuracy to which the surfaces were cut was well within 10 minutes of the desired directions even after polishing. The prisms were 13 mm. high and the faces were nearly as wide as high, the polish being as perfect as that of quartz or calcite.

The results are found to be in full accordance with the author's general explanation given in 1908. At the temperature of the production of the uniaxial interference figure of circular coloured rings and rectangular black cross, as observed with the plate perpendicular to the first median line in convergent polarised light, two of the refractive indices (as observed with the prisms) become equal, namely, the two,  $\alpha$  and  $\beta$ , which are closest together at the start. For, on heating the prism affording these two indices, the two signal images in monochromatic light, already so close together that the corresponding spectra in white light overlap, approached each other and became identical (superimposed) between  $90^\circ$  and  $100^\circ$  C. whatever was the colour of the light employed; while at  $105^\circ$  they had perceptibly passed each other and  $\alpha$  had become  $\beta$  and *vice versa*, the differences of the indices themselves being 0.0004.

The phenomena cannot be followed with safety beyond this temperature, owing to the probability of decomposition into plaster of Paris. But at the temperature of the observations ( $105^\circ$ ) no trace of decomposition had occurred, and although the experiment was repeated on another day, no fracture of the relatively large and valuable prism occurred. The same fortunate result attended the observation with the prism affording  $\beta$  and  $\gamma$ , which was employed for determinations at the same temperatures, in order to obtain a complete record of all three indices for each temperature. This happy result

\* 'Wien. Akad. Ber.,' 76, vol. 2, p. 793.

was secured by very slow heating and subsequent cooling, in the most recent form of spherical crystal-heating air bath provided by Fuess for use with the large model (No. 1a) spectro-refractometer which was used throughout the determinations, the monochromatic light being supplied by the author's spectroscopic monochromatic illuminator, on the entrance slit of which the light from an electric lantern was focussed. The thermometer employed was one which had recently had its fixed points redetermined, and its cylindrical bulb was almost touching the crystal-prism.

The optic-axial-angle measurements of the apparent angle in air, 2E, the apparent acute angle in monobromnaphthalene, 2Ha, both made with the plate perpendicular to the first median line, and of the apparent obtuse angle in monobromnaphthalene, 2Ho, made with the plate cut normal to the second median line, were carried out with the larger Fuess axial angle apparatus also fed by monochromatic light from the illuminator. The true angle within the crystal between the optic axes, 2Va, was calculated by the usual formula,  $\tan Va = \sin Ha / \sin Ho$ . But it was also determined directly by immersing the plate perpendicular to the first median line in pure monochlorobenzene, whose refractive index for sodium light (1.5248) is almost absolutely identical with the mean of the three indices of the crystal (1.5245). The observations of 2E at higher temperatures with the first plate were performed in the heating arrangement with plate-glass windows (optically worked) provided with the Fuess apparatus. The temperatures superior to the ordinary were in all cases corrected for the conduction of the crystal holder, which was of platinum-iridium in order to reduce it to a minimum, the correction being determined by replacing the crystal under like conditions by the bulb of a very small thermometer. This is a most necessary correction, amounting to  $7^\circ$  in the neighbourhood of  $100^\circ$ .

The extinction directions were determined with the Fuess stauroscope, forming part of the Groth universal crystal apparatus, and full corrections were made for the zero of the Nicols by reversals of the crystal, and for the setting of the crystal edge to the optically-worked edge of the glass carrier plate by accurate goniometrical measurements.

The results are as follows:—

*Orientation of the Optical Ellipsoid.*—Determinations of the extinction directions in the symmetry plane, made both with the whole original crystal and with the end-piece A (fig. 3), agree in indicating that for sodium light at  $12^\circ$  the first median line is inclined  $37^\circ 42'$  to the normal to the edge  $pp = 110:1\bar{1}0$ , or to the normal to the face  $a(100)$ , and  $46^\circ 40'$  to the axis  $a$ ; the second median line makes the same angle of  $37^\circ 42'$  with the vertical  $c$ -axis of the crystal, while the first median line is inclined  $52^\circ 18'$

to the  $c$ -axis. This will be clear from both fig. 2 and fig. 3. The first median line lies in the obtuse angle of the crystallographic axes  $a$  and  $c$ .

The results for other colours of the spectrum were not perceptibly different.

Miers\* gives  $37^{\circ} 30'$  as the most trustworthy value derived from previous observers for the inclination of the first median line to the normal to  $a(100)$ , a difference from the author's value which is almost within the error of stauroscopical measurements.

*Refractive Indices.*—The following table expresses the combined results of the determinations, by the method of minimum deviation, with both prisms, for the uniform temperature of  $12^{\circ} \text{C}$ , a constancy to within half a degree of this temperature having been maintained on both days. It takes  $2^{\circ}$  to influence the refractive index one unit in the fourth place of decimals. The two values of  $\beta$ , derived from the two prisms, never differed by more than two units in the fourth place, and for four of the seven wave-lengths for which observations were made the values were absolutely identical. This is an eloquent testimony to Hilger's accurate cutting, and to the trustworthy character of the measurements. The angle of the prism affording  $\alpha$  and  $\beta$  was  $60^{\circ} 20'$ , and of that yielding  $\beta$  and  $\gamma$   $59^{\circ} 54'$ .

Refractive Indices of Selenite at  $12^{\circ}$ .

	$\alpha$ .	$\beta$ .	$\gamma$ .
Li line .....	1.5178	1.5201	1.5270
C " .....	1.5184	1.5207	1.5276
Na " .....	1.5207	1.5230	1.5299
Wave-length 578 ...	1.5213	1.5237	1.5307
Tl line .....	1.5231	1.5255	1.5325
F " .....	1.5262	1.5285	1.5355
G " .....	1.5303	1.5328	1.5400

The values obtained by von Lang for four of the above wave-lengths at  $16^{\circ} 8$  were as under, only those for  $\beta$ , however, being strictly comparable as directly determined.

	$\alpha$ .	$\beta$ .	$\gamma$ .
C line .....	1.5183	1.5204	1.5281
D " .....	1.5208	1.5229	1.5305
F " .....	1.5263	1.5283	1.5360
G " .....	1.5309	1.5328	1.5407

The agreement with the author's values is wonderfully close in the case of

\* 'Mineralogy,' p. 526.

$\beta$ , taking into account the effect of the slight difference of temperature, which is to add 0.0002 to von Lang's values in order to correct them to 12°.

Determinations were made for the particular wave-length 573 in the greenish-yellow, because this was found to be the interesting and important wave-length for the maximum which the optic axial angle has been shown by von Lang to possess, but which he was unable to locate nearer than the D line, an exceptional phenomenon which it is important to study with precision. With the aid of the monochromatic illuminator it is quite easy to observe and demonstrate the maximum, and to determine its position with an accuracy hitherto unattainable. It was assumed by von Lang to occur for the sodium ray D, one of the six spectrum rays employed by him in his observations, because among these six values it was the highest. The crystal under discussion showed the maximum optic axial angle at wave-length 573 slightly on the green side of D, so that von Lang's observation is confirmed, and the exact position allocated more closely owing to the use of the monochromatic illuminator.

Refractive Indices of Selenite at 105°.

	$\alpha$ .	$\beta$ .	$\gamma$ .
Li line .....	1.5154	1.5158	1.5243
C " .....	1.5160	1.5164	1.5249
Na " .....	1.5184	1.5188	1.5274
Wave-length 573 ...	1.5190	1.5194	1.5280
Tl line .....	1.5209	1.5213	1.5300
F " .....	1.5239	1.5243	1.5330
G " .....	1.5285	1.5289	1.5377

The direction corresponding to  $\gamma$  is the same as at the ordinary temperature, but  $\alpha$  and  $\beta$  are now reversed, the values given as those of  $\alpha$  corresponding to the direction which at 12° afforded  $\beta$ , that is, the direction of the symmetry axis  $b$ , and *vice versa* as regards  $\beta$ .

The amount of double refraction is not appreciably altered by the rise in temperature. Thus the difference of the  $\alpha$ - and  $\gamma$ -indices for sodium light at 12° is 0.0092, and at 105° it is 0.0090, practically the same. But the reduction in refractive power, the usual accompaniment of rise of temperature in crystals, is very unequal for the three directions. Between 12° and 105° the refractive index along the direction which affords  $\alpha$  at 12° (the second median line) becomes reduced by 0.0019; along the direction of the symmetry axis, affording  $\beta$  at 12°, it is reduced by 0.0046; and along the direction of the first median line, which affords  $\gamma$  at all temperatures, the reduction is 0.0025. Thus, while the general drift of the change of refraction is to

become lower as the temperature rises, the symmetry axis value  $\beta$  oversteps the second median line value  $\alpha$  in amount of reduction, rendering the former now the minimum,  $\alpha$ ; thus  $\alpha$  and  $\beta$  interchange positions. This crossing over of these two indices is shown to scale in fig. 4, which gives a very clear expression of the whole of the movement of the Welsby signal images, the movement of  $\alpha$  and  $\beta$  being given by one prism, and that of  $\beta$  and  $\gamma$  by the other, the two effects being combined in the diagram. The three upper images are arranged according to their relative positions at  $12^\circ$ , and the three lower are as they actually appear at  $105^\circ$ .

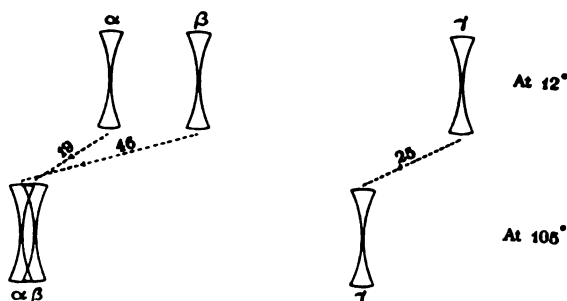


FIG. 4.

It was very interesting to see the interchange in progress as the prism affording  $\alpha$  and  $\beta$  was heated. At  $12^\circ$  the circle-reading separation of the two images was  $12'$ , at  $37^\circ$  the difference had become reduced to  $10'$ , at  $50^\circ$  to  $7'$ , at  $63^\circ$  to  $6'$ , both images moving also steadily in the direction of reduced deviation. At  $80^\circ$  the two images were only  $3'$  separated, and at  $90^\circ$  they were superimposed, one extinguishing at  $0^\circ$  of the Nicol and the other at  $90^\circ$ , so that the appearance was as of a single image of unpolarised light, although there were really two images polarised in planes at right angles. No difference of relative position could be clearly made out until the temperature of  $100^\circ$  was reached, but for  $105^\circ$  they were distinctly separated on the other side of each other to the extent of  $2'$ . This is precisely the same phenomenon as was observed with the other cases of crossed-axial-plane dispersion investigated by the author, so that there can be no doubt concerning the fact that a common explanation applies.

*Optic Axial Angle.*—The following values for the apparent angle in air,  $2E$ , were obtained for the temperature of  $11^\circ.5$ , with the plate perpendicular to the first median line.

The maximum angle was clearly proved to occur when the circle-reading of the monochromatic illuminator was such as corresponded on the wave-length curve to the wave-length 573, sodium light corresponding to 589 and thallium light to 535.

## 2E of Selenite at 11°5.

Li .....	99° 16'	Tl .....	100° 34'
C .....	99 27	F .....	99 58
Na .....	100 36	G .....	98 24
Wave-length 573 ...	100 43		

The true angle within the crystal, 2Va, will next be given for two ordinary temperatures, 8° and 10°, derived from measurements of the apparent acute angle 2Ha and apparent obtuse angle 2Ho with the plates perpendicular to the first and second median lines respectively, immersed in monobrom-naphthalene. The temperature was maintained within half a degree of constancy at 8° or at 10° for each pair of observations used in combination for the calculation of the true angle at that temperature, by the formula already quoted.

## True Optic Axial Angle 2Va of Selenite.

	At 8°.	At 10°.
Li .....	61° 14'	60° 27'
C .....	61 18	60 31
Na .....	61 45	61 1
Wave-length 573 ...	61 47	61 4
Tl .....	61 32	60 51
F .....	61 12	60 34

The same wave-length 573 is again found to be that corresponding to the maximum true angle.

It is interesting that the liquid monochlorbenzene, of which a very pure sample was kindly placed at the author's disposal by Dr. Veley, F.R.S., has precisely the same refractive index for sodium light as the mean index (mean of  $\alpha$ ,  $\beta$ , and  $\gamma$ ) of selenite, the exact respective numbers being 1.5248 and 1.5245. Hence the value of the true angle in the neighbourhood of the sodium line, including wave-length 573, may be very accurately determined, and for the ends of the spectrum also approximately, by immersing the plate perpendicular to the first median line in that liquid, and thus a most valuable means of directly determining the wave-length for the maximum true angle is afforded. The following values were obtained in this manner for the temperature of 8°5:—

## 2Va of Selenite directly determined at 8°5.

Li .....	60° 57'
C .....	61 3
Na .....	61 28
Maximum angle observed for wave-length 573...	61 30
Tl .....	61 19
F .....	60 46
G .....	60 0

The maximum was thus clearly proved by both methods to be at wave-length 573. Additional measurements were made for short intervals corresponding to a very few units of wave-length on each side of 573, and the maximum definitely located for 573.

In all these measurements the readings for the axes themselves indicated that the first median line moved in the symmetry plane towards the axis *c* 5 minutes between Li and wave-length 573, and then moved back again towards the axis *a* for 20 minutes between 573 and G. Hence 573 is also a limiting wave-length for the position of the first median line in the symmetry plane.

The results of the measurements of the apparent angle in air, 2E, at two higher temperatures will now be given, and they will be followed by a record of the precise temperature for each wave-length for which the uniaxial rectangular cross and circular rings are produced.

#### 2E at Higher Temperatures.

	At 48° (corr.)	At 75° (corr.)
Li.....	74° 26'	52° 14'
C .....	74 40	52 30
Na .....	75 40	54 18
Wave-length 573 ...	76 5	54 55
Tl .....	75 23	54 22
F .....	74 48	52 40

The maximum still remains at wave-length 573 on heating, as will be obvious from the above table.

#### Corrected Temperatures for the Production of the Uniaxial Figure by Selenite.

G .....	102°·5
F .....	104°·5
Tl .....	105·1
Last wave-length for which uniaxial figure is produced, wave-length 573...	105·5
Na .....	105·2
C .....	104·7
Li .....	104·5

The cross is first formed for G-light, as the temperature rises above 100°, hence the usual order of the spectrum is reversed in the above table. The uniaxial figure is next produced simultaneously for both F and Li-light, while for wave-lengths between F and G the axes are separated in the new plane, the vertical, if the section-plate were arranged for the axes to be

separated horizontally at the ordinary temperature as usual. For the parts of the spectrum between Li and F they still remain in the horizontal plane. But as the temperature rises further, successive parts of the spectrum, approaching the centre from either end, produce the crossing; thus at  $105^{\circ}$  thallium light and sodium light produce it, while the axes remain still separated appreciably in the horizontal plane for the greenish-yellow part between, and while for spectrum colours outside either Tl green or Na yellow the axes are vertically separated, and the more so the nearer the end of the spectrum. Finally, for wave-length 573 in the greenish-yellow, the uniaxial figure is produced at a temperature of  $105^{\circ}5$ , and on rotating the prism circle of the spectroscopic monochromatic illuminator either way, so as to feed the convergent light polariscope with light on either side of wave-length 573, the rectangular cross begins to open out into hyperbolic brushes again, and in both cases in the vertical plane, the axes becoming separated more and more in that plane as either end of the spectrum is approached. Just near wave-length 573 the horizontal spider-line appears as a common tangent to the two vertices of the hyperbolic brushes, the one vertex being below and the other above the spider-line. They come into contact with the spider-line and with each other, and produce a rectangular cross with arms at  $45^{\circ}$  to both horizontal and vertical spider-lines, at the critical wave-length 573 itself, and recede away as hyperbolæ above and below the spider-line as the wave-length of the light is altered in either direction. In a similar manner, at the lower temperature of  $104^{\circ}5$ , the vertical spider-line appears as a tangent to the hyperbolic vertices for Li or F-light (for which the vertices and spider-line touch and the brushes join up to make the rectangular cross), while on altering the wave-length towards the centre of the spectrum, from either Li or F, the vertices recede right and left from the spider-line along the horizontal diameter. But if the spectrum is moved away from F towards the violet (in the case of Li, of course, we almost at once get out of the visible spectrum) the vertices separate along the vertical diameter. For temperatures superior to  $105^{\circ}5$  the axes are separated in the vertical plane for all wave-lengths, but the minimum separation is for wave-length 573.

These observations with the Hilger plate perpendicular to the first median line were repeated the next day with identical results. The temperatures actually read on the thermometers were, as already explained,  $7^{\circ}$  higher than those given in the table, as the correction for conduction already referred to amounts to as much as  $7^{\circ}$ . This important correction appears to have been neglected in the work of previous observers.

The fact that the critical wave-length, on either side of which at  $105^{\circ}5$



the axes are separated in the vertical plane, is 573, affords another strong confirmation of the accuracy of the conclusion that this is the wave-length corresponding to the maximum optic axial angle, for the determination of the tangential limiting position was one of considerable refinement and certainty with the monochromatic illuminator, the plate perpendicular to the first median line affording very sharp brushes, being 2 mm. thick. The two parallel surfaces were 14 mm. by 13 mm. in size.

During the heating it was confirmed that the first median line moves in the symmetry plane towards the axis  $a$  about  $5\frac{1}{2}^\circ$ , as noticed by former observers. Between  $20^\circ$  and  $95^\circ$  C., von Lang observed  $5^\circ 38'$  of movement. For the same interval the author observed  $5^\circ 41'$ .

After having completed the work on the crystal in question, it was considered desirable to determine the temperatures of crossing of the optic axes with other plates from distinct crystals, and three were experimented with, for two of which the author's thanks are due to Messrs. Newton. All three were small plates, prepared by Steeg and Reuter, mounted in the manner described on p. 41. The results for all three are given in the next table, the temperatures being corrected for conduction as in the case of the Hilger section-plate.

Temperatures of Crossing for Three other Plates.

	Plate 1.	Plate 2.	Plate 3.
G .....	106°	111°	108°
F .....	108	113	110
Tl. ....	109	114	111
Wave-length 573 ..	110	114·5	111·5
Na .....	109·5	114·2	111·3
C .....	108·5	113·2	110·3
Li .....	108	113	110

The temperature will thus appear to vary for different crystals, although, including the Hilger section-plate, the variation does not exceed  $9^\circ$ . This amount, however, is sufficient to fully justify the author in having cut the whole of the prisms and section-plates for this work out of one and the same crystal. The wave-length for the maximum temperature was in all cases 573.

*Conclusions.*—The experimental work on selenite now described confirms the author's previously published conclusion, derived from other examples, that the phenomenon of crossed-axial-plane dispersion is due to very low double refraction, combined with close approximation of the intermediate index of refraction to one of the extreme indices, and to the fact that change

of wave-length of the light or change of temperature, or both, cause the intermediate index to approach still nearer to the extreme one in question until it becomes identical with it, and eventually to pass it, the relative positions of the two indices thus becoming reversed. The uniaxial rectangular cross and circular rings are produced at the critical point of identity. This critical point is a function of both wave-length and temperature, being a fixed one only for a particular wave-length and specific temperature. The temperature has a maximum for wave-length 573 on the greenish-yellow side of the D lines (589). The optic axial angle has a maximum for the same wave-length 573, for all temperatures below that of the crossing of the optic axes, and a minimum for temperatures superior thereto up to the temperature of decomposition ( $120^{\circ}$ ) of selenite. The change of orientation of the median lines (bisectrices of the optic axial acute and obtuse angles) within the symmetry plane, at any specific temperature, also exhibits a critical limit for this greenish-yellow light of wave-length 573, which is thus a very important radiation in connection with the optics of selenite. The range of temperature which includes the production of the uniaxial figure for all colours of the spectrum does not exceed  $4^{\circ}$ , varying in different crystals from  $3^{\circ}5$  to  $4^{\circ}$ . The absolute temperatures of crossing for the four crystals investigated varied  $9^{\circ}$ , the maxima (for wave-length 573) varying from  $105^{\circ}5$  to  $114^{\circ}5$ , corrected for conduction of crystal holder.

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*The Electrolytic Properties of Dilute Solutions of Sulphuric Acid.*

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(Received June 4,—Read June 18, 1908.)

Part 1.—By W. C. D. WHETHAM.

1. *The Electrical Conductivities.*

The first section of the present paper contains an account of a continuation of the work described in the 'Proceedings of the Royal Society,' A, vol. 76, p. 577, 1905, and a statement of the object of the investigation may be reproduced from that place :

"If the measure of the electrical conductivity of a solution be divided by that of the concentration expressed in gramme-equivalents per unit volume, we obtain a quantity which may be called the equivalent conductivity of the solution. If the conductivity of the solvent used be subtracted from that of the solution, the corresponding quantity may be taken as giving the equivalent conductivity of the solute.

"As is well known, the equivalent conductivity of neutral salts when dissolved in water approaches a limiting value as the dilution is increased, and, in terms of the ionisation theory, this limiting value corresponds with complete ionisation.

"With solutions of acids and alkalies, however, the phenomena are different. As dilution proceeds, the equivalent conductivity reaches a maximum at a concentration of about a one-thousandth or a two-thousandth of a gramme-equivalent per litre, and then falls rapidly as the dilution is pushed farther.

"It has been supposed that this diminution of equivalent conductivity at extreme dilutions is due to interaction between the solute and the impurities which remain even in redistilled water.

"Kohlrausch has given evidence to show that the chief impurity in water carefully redistilled is carbonic acid," but the experiments described in the writer's former paper show that no appreciable change in the phenomenon is produced by boiling the water used as solvent repeatedly under low pressure, and re-admitting the air through potash bulbs. This process would remove a great part at least of the carbonic acid in the solvent, and it causes a large diminution in the conductivity of the water, but, on adding small

quantities of sulphuric acid to solvent so purified, a conductivity curve of the normal type is obtained—the lowering of equivalent conductivity at great dilution is not affected appreciably. The first step in continuing the research consisted in repeating the process of boiling the solvent under diminished pressure, but in re-admitting air through bulbs containing dilute sulphuric acid as well as others containing potash. Any volatile alkaline impurity such as ammonia would thus partly be removed, and, if such impurity were the cause of the phenomenon, the conductivity curves obtained by adding acid to the purified solvent would be modified.

The following results were obtained—

Number of solution.	Concentration (gramme-equivalents per 1000 grammes of solution = $m$ ).	$m^{\frac{1}{2}}$ .	Conductivity at 18° C. in arbitrary units = $k$ .	Conductivity less that of solvent = $k_0$ .	Equivalent conductivity of sulphuric acid = $k_0/m$ .
0	0.0	—	$1.041 \times 10^{-3}$	—	—
1	$4.812 \times 10^{-4}$	0.03638	$1.800 \times 10^{-4}$	$1.696 \times 10^{-4}$	3.526
2	$9.158 \times 10^{-4}$	0.04506	$3.542 \times 10^{-4}$	$3.438 \times 10^{-4}$	3.757
3	$1.988 \times 10^{-3}$	0.05881	$7.817 \times 10^{-4}$	$7.718 \times 10^{-4}$	3.890
4	$3.579 \times 10^{-3}$	0.0710	$1.418 \times 10^{-3}$	$1.408 \times 10^{-3}$	3.936
5	$6.523 \times 10^{-3}$	0.0985	$2.543 \times 10^{-3}$	$2.533 \times 10^{-3}$	3.910

As comparative numbers only were needed, the conductivities were expressed in arbitrary units—the reciprocals of the measured resistances in the cell employed. It will be seen that the usual phenomenon of a fall in the equivalent conductivity at great dilution is still evident, and the curve obtained by plotting  $m^{\frac{1}{2}}$  and  $k_0/m$  is not appreciably different from that obtained when unboiled distilled water is used as solvent.

Thus the efforts made to remove residual ammonia are without result on the conductivity of solutions of sulphuric acid made up with the solvent so purified.

Hence it seems that traces in the solvent neither of carbonic acid nor ammonia are competent to explain the peculiarities in the conductivity of dilute solutions of acids. As will be pointed out in Part 2 of this paper, however, another possibility remains, namely, the presence in redistilled water of traces of carbonate or bicarbonate of ammonia. Such an impurity might produce the effect observed both with acids and with alkalis, and the slight trace of it requisite might not be removed by treatment such as is described above. However this may be, it seems unlikely that the impurity which is usually assumed to be the cause of the phenomenon is competent to explain it.

## 2. *The Transport Ratios.*

If the phenomenon of the decrease in equivalent conductivity be not due to impurities in the solvent, it must be caused by some change in the conductivity of the solute itself. A decrease in conductivity must be accompanied by a decrease in the effective velocity of one or both of the ions. Since the phenomenon under investigation occurs with alkalis as well as acids, it seems likely that, if it be not due to impurities, it depends on the presence of the one ion in each of these classes of compounds which is identical with one of the ions of the solvent—in acids the hydrogen ion, and in alkalis the hydroxyl ion. Hence, on the supposition we are now making, it is probable that one ion would be affected in a different way to the other. We may expect that in solutions of acids the hydrogen ion travels slower at great dilutions than at more moderate concentrations. Such a differential treatment of the ions would be made manifest by a determination of the migration constant or transport ratio of solutions of different concentrations. If an electric current be passed through a solution between non-dissolvable electrodes, solute is lost from the solution in the neighbourhood of both electrodes, and it is readily shown that the ratio of loss is equal to the ratio between the opposite ionic velocities. The ratio of the velocity of the anion to the sum of the velocities is taken as the transport ratio or migration constant. A decrease in the velocity of the hydrogen ion of acids, then, would cause an increase in the measured transport ratio.

The transport ratio usually has been measured by determining the concentration of the solution by chemical means before and after the passage of the current in the neighbourhood of the two electrodes. But, in the present case, the concentrations involved were far too small to be estimated chemically; it was necessary to devise a new method.

Now, in the measurement of electrical conductivity, we possess a means of determining the concentration of a dilute solution much more sensitive and accurate than any method of chemical analysis, and a method of experimenting was designed to utilise these advantages.

Fig. 1 shows a cell made of Jena glass. It consists of two vertical tubes connected horizontally through an inverted **V**, to the apex of which a quill tube of glass is fused. To this quill tube is fixed a piece of rubber tubing, and by a slight increase of air pressure the level of the liquid in the inverted **V** can be depressed so as to separate the liquid into two parts, one confined to each vertical limb of the apparatus.

In each vertical tube are placed two platinum electrodes, carried by glass tubes through the ends of which stout platinum wires are sealed. By

measuring the resistance between these electrodes, the specific resistance of the solution round them can be determined, while, if each pair of electrodes is connected electrically together, a current may be passed through the whole apparatus from one pair of electrodes to the other when the liquid fills the inverted V-tube as well as the vertical limbs.

The electrodes in the side tubes lie just above the junctions with the connecting tube. By this arrangement the danger of convection currents, leading to a mixture of the anode and cathode portions of the solution, is avoided, for, in the cathode region, where the concentration diminishes, the lighter liquid rises towards the surface, while the denser anode liquid has no tendency to pass into the rising connecting tube, and sinks to the bottom of the side limb of the apparatus. The influence of diffusion was shown to be negligible in the course of the experiments, for identical results were obtained in similar experiments of long and short duration, in which the effects of diffusion would differ.

The mode of procedure is as follows: A solution of pure potassium chloride is made up of a convenient strength by weighing out the salt. This solution is diluted by adding a known weight of water. The resistance of the solution so prepared, when

placed in the cell, is measured between each pair of electrodes. From the specific resistance of potassium chloride solutions, as given by Kohlrausch, this gives the cell constant of each end of the apparatus, treating each vertical limb as a separate resistance cell. After careful washing, the apparatus is then filled with a solution of sulphuric acid, the concentration of which is known to be approximately that required. By measuring the resistance between each pair of electrodes, two values for the exact concentration may then be calculated from Kohlrausch's tables.

The apparatus is now ready for a migration experiment. A current from

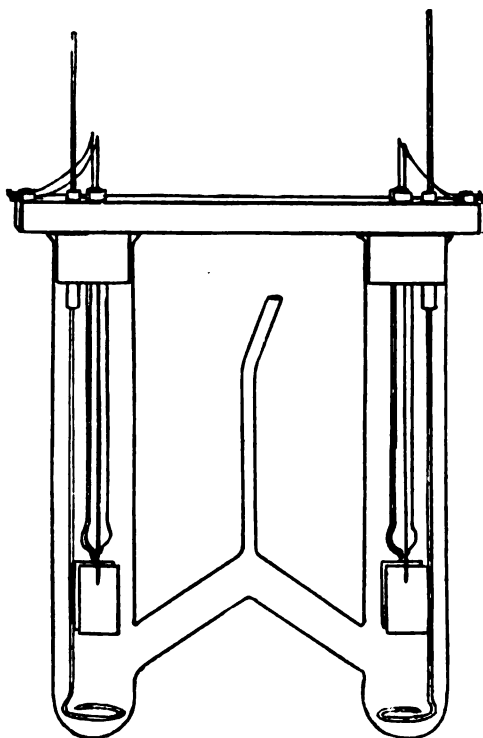


FIG. 1.

a battery of 50 or 100 small storage cells is passed through the apparatus from one pair of electrodes to the other, each pair, in this part of the work, being used as a single electrode. The strength of the current is determined by passing it through a standardised shunted galvanometer, and thus the total amount of chemical decomposition calculated from the known values of the electro-chemical equivalents. After a definite time has elapsed, the circuit is broken, the two parts of the solution are separated by increasing the pressure of the air in the inverted V-tube, and measurements are taken of the resistance between each pair of electrodes as before. The change in concentration in the solution round each electrode may thus be estimated, and, by extracting and weighing each part of the solution, the total change in contents of acid calculated.

In a solution of sulphuric acid, the ions are hydrogen and the sulphion group  $\text{SO}_4$ . Hydrogen is liberated as such at the cathode, but the sulphion reacts with the water to form sulphuric acid and oxygen, the latter escaping. Thus when one gramme-equivalent of hydrogen is evolved, one gramme-equivalent of acid is reformed at the anode by the secondary action of the sulphion and the water. But, besides this change, that due to migration must be considered. If the cation of any salt solution drifts one way with a velocity  $u$ , and the anion the other with a velocity  $v$ , the amount of separation in unit time is  $u+v$ . In accordance with the principle of migration, there is a loss of salt measured by  $v$  at the cathode, and a loss measured by  $u$  at the anode. But in our case there is also a gain of  $u+v$ , equal to the total amount of decomposition, at the anode. Thus the resultant gain at the anode is  $u+v-u$  or  $v$ , and the resultant loss at the cathode is also  $v$ . Hence, by determining the loss and gain, we get two independent values for the same quantity, and the concordance between them gives a preliminary test of the success of the apparatus and method.

Finally, a knowledge of the value of the current and its time of flow gives  $u+v$ , and enables us to calculate  $v/(u+v)$ , the transport ratio.

After some changes, the apparatus in its final form gave satisfactory results as tested by the agreement between the loss of acid at the cathode and the gain at the anode. Details of one experiment may be given as an example.

Resistances before passage of current	{	Anode vessel ... 7102, 7106, 7112 = 7107 mean in ohms
		Cathode „ ... 6252, 6258, 6264 = 6258 mean in ohms.

Current from 50 cells (= 100 volts) passed for 15 minutes—

Resistances... { Anode vessel, 8316, 8263, 8296 = 8297  
Cathode „ 5452, 5461, 5464 = 5462

Weight of solutions in anode vessel = 53.25 grammes.

Weight of solutions in cathode „ = 57.00 „

From these results it follows that the conductivity of the solution before the passage of the current was  $1.408 \times 10^{-5}$ .

After the passage of the current the conductivity of the anode solution was  $1.614 \times 10^{-5}$ , and of the cathode solution  $1.219 \times 10^{-5}$ .

The concentration of the original solution was  $4.042 \times 10^{-5}$  gramme-equivalent per 1000 grammes. From the known curve between concentration and equivalent conductivity, the concentration of the final anode and cathode solutions was estimated as  $4.575 \times 10^{-5}$  and  $3.546 \times 10^{-5}$  respectively. Then, from the observed total masses of their solutions, the total gain and loss in contents was calculated as  $2.843 \times 10^{-7}$  gramme-equivalent and  $2.831 \times 10^{-7}$  gramme-equivalent respectively.

A rough estimate of the current gave  $1.491 \times 10^{-4}$  ampere, and, as the total number of gramme-equivalents liberated,  $1.390 \times 10^{-6}$ . Thus the transport ratio is approximately  $0.2836/1.390 = 0.205$ .

No stress can be laid on this last result, as the method of measuring the current was not that finally adopted as satisfactory, but the concordance between the gain of acid at the anode and the loss at the cathode showed that, so far, the method was successful.

At this point the pressure of other duties prevented the writer from continuing the experiments, but, by the aid of the Government Grant Committee of the Royal Society, the services of Mr. H. H. Paine were secured. The work described in Part 2 of this paper is Mr. Paine's; the present writer only exercised a general supervision over the course of the research.

## Part 2.—By H. H. PAINE.

### 1. *Method of Experiment.*

The migration constant was determined for solutions of sulphuric acid of concentration varying from 0.1 to 0.00005 normal. A current, the strength of which was determined by means of a standardised galvanometer, was passed through the migration cell, and the total change in the quantity of solute round the anode and cathode measured. As explained in the first part of this paper, the value of this change in gramme-equivalents, divided by the number of gramme-equivalents of hydrogen evolved at the cathode, gives us the migration constant for the solution.



The great advantage of sulphuric acid for these experiments is that no uncertain reactions take place at either anode or cathode. Measurements of the change in concentration at the two electrodes are thus equally trustworthy, and each serves as a check on the other.

The solutions used were made up with water having a specific conductivity of from  $0.9 \times 10^{-6}$  to  $1.0 \times 10^{-6}$  reciprocal ohm at  $18^{\circ}$  C. Ordinary distilled water was redistilled in a Jena glass apparatus with a trace of sulphuric acid and of potassium bichromate. A stock solution of sulphuric acid (of strength about 0.1 normal) was prepared from some pure 50 per cent. sulphuric acid supplied by Messrs. Baird and Tatlock. The conductivity of this solution was measured, and its exact strength thence determined by means of Kohlrausch's tables. Dilute solutions were obtained from this by taking a weighed quantity and adding the requisite amount of water.

After the passage of the current through the migration cell, the strengths of the solutions in the anode and cathode regions were determined by measuring their conductivities. For this purpose it is necessary to know how the conductivity varies with concentration. The relation between the two has been determined by several observers, and the results plotted in the form of a curve showing the ratio of the equivalent conductivity to the cube root of the concentration. It was thought advisable, however, to have such a curve for the actual solution under observation. Since the solutions were all made up gravimetrically from the original one, we have at once a means of finding the concentration (in terms of that of the original). The conductivity was also measured. Each solution made up thus gave a point on the curve. From the curve so drawn, calculations were made for determining the strengths of the two solutions after the passage of the current. Slight effects due to the solution of impurities during the course of the experiment would give too small a value for the change in concentration on the one side, and too large a value on the other; taking the mean, therefore, tends to eliminate these effects; agreement between the changes on the two sides is a sure test that such errors have not entered to vitiate the results. This is a very important consideration, for with such weak solutions as were used, fouling, not only by the solution of solid matter from the surface of the vessel, but also by the absorption of gases such as ammonia from the air, is very likely to occur. Without such a check it would be dangerous to draw any conclusions as to the value of the migration constant for solutions weaker than 0.0001 normal, whereas with the help of this check successful experiments were conducted with solutions as weak as 0.00005 normal.

2. *Apparatus.*

1. *Conductivity Cells.*—Two cells were used in the course of the experiments for the purpose of measuring the conductivity, one for the two strongest solutions (0.1 and 0.01 N.) and the other for solutions of strength 0.001 N. and under.

The electrodes in both cells were of platinum, but in the case of the cell used for the stronger solutions (fig. 2), they were coated with platinum-black, while in the other cell (fig. 3), after platinisation, they had been heated to redness before being sealed into the glass. In the second cell, contact with the electrodes was made by means of mercury poured into the side

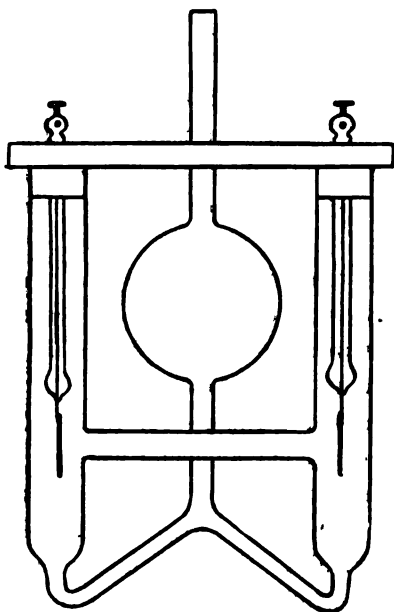


FIG. 2.

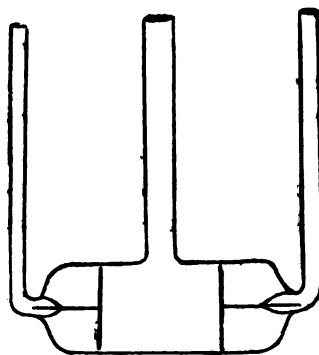


FIG. 3.

tubes. The centre tube leading to the cell-chamber was closed with a glass cap, by the use of which, it was found, fouling from the atmosphere was prevented completely.

The cell-constant for each cell was determined by means of a standard potassium chloride solution made up from the carefully prepared, pure, crystallised salt. Knowing the concentration of this solution, we can calculate its conductivity (in reciprocal ohms) from the tables compiled by Kohlrausch.

The resistance in each case was determined by the method of Wheatstone's bridge. By the use of the commutator described in a paper by one of the

authors,\* an alternating current was obtained, and at the same time a galvanometer used for testing the balance. The commutator was driven at the requisite speed by means of a small electric motor. In all measurements of the resistance the cell was placed in a bath of water kept well stirred and maintained at a temperature of  $18^{\circ}\text{C}$ ., as shown by a Beckmann thermometer reading to hundredths of a degree. The temperature of the solution was regarded as constant and uniform when the measured resistance remained unaltered with time.

2. *The Migration Cell*.—This has been described in the first part of the paper. It may further be noticed here that by placing a pair of electrodes on each side, it was possible to measure the resistances of both portions of the liquid immediately before and immediately after the passage of the current, without transference to other conductivity cells. An almost certain cause of fouling was thus avoided. This device could be employed only for the weaker solutions (0.0002 N. and under), as the resistances in the case of stronger solutions would be too small to be measured accurately with these electrodes. But with the stronger solutions any possible fouling on transfer would be inappreciable.

3. *Galvanometer*.—The current through the migration cell was measured by means of a Nalder's moving-coil galvanometer, which, with the shunts used in the experiment, was previously standardised. This was done in the following way:—A current from a single storage cell (with a suitable resistance in series) was passed through a milliampere- (or volt-) metre, of resistance exactly 1 ohm. The terminals of the galvanometer were connected with the terminals of the ampere-metre through convenient resistances. From the reading of the ampere-metre and a knowledge of the resistance in the galvanometer circuit, we can calculate the current through the galvanometer. The deflections of the suspended coil of the galvanometer (observed by the ordinary reflection method) were noted simultaneously.

### 3. *Experimental Details.*

The method of procedure for solutions of strengths 0.0005 normal and over differed slightly from that for weaker solutions. In the case of the stronger solutions the conductivity was too great for the resistance to be measured by means of the electrodes in the migration cell. Hence the liquid had to be transferred to a conductivity cell. The conductivity of the original solution was first determined in one of these cells, in order to obtain a point on the equivalent conductivity curve. Some of the solution was then poured into the migration cell until the connecting tube was completely

\* 'Phil. Trans.,' A, 1900, vol. 259, p. 321.

filled. The current (supplied by a hundred small storage cells) was passed through the apparatus for a time (generally 10 to 15 minutes) sufficient to produce on the average a 10 per cent. change in the strength of the solutions, that is to say, until 10 per cent. of the sulphate ions on the cathode side had migrated to the anode region. When the current had been stopped, the air pressure in the inverted V-tube was raised until the liquid had been forced to the ends of the tube, thus separating the anode and cathode portions. Each portion was then well stirred, and afterwards transferred by means of a syphon to a weighed flask, the syphon and flask having been carefully rinsed with pure water, and dried, before using. After the weight had been taken, the solution was poured into the conductivity cell, and its resistance measured.

For solutions weaker than 0.0005 normal, the initial conductivity was determined in the conductivity cell as before. After the solution had been poured into the migration cell, the air pressure in the inverted V-tube was raised until the liquid had descended to the ends of the tube. The resistance on each side was measured, the solution being well stirred, and the temperature maintained at 18° C. After the air pressure had been released, and the liquid had risen to its former level, the current was passed through for the required time. The anode and cathode portions were again separated, as at the beginning of the experiment, and the resistances measured. Finally, the two portions were separately drawn off by means of a syphon, and weighed. The final conductivities are easily calculated, from the fact that they bear to the initial conductivity the ratios of the resistances (measured in the migration cell) at the beginning to those at the end of the experiment.

In calculating the conductivity of the sulphuric acid, the conductivity of the solvent was deducted from that of the solution in every case.

#### 4. *Experimental Results.*

The following example shows the complete method of calculation for one of the experiments:—

##### *Solution 20.*

Original strength (as made up from a standard solution).....	$1.0140 \times 10^{-2}$ grm.-equiv. per c.c. ( $= m_0$ )
Resistance in conductivity cell .....	12,916 ohms
Cell-constant.....	0.4532
Conductivity of solution.....	$\frac{0.4532}{12916}$
	$= 3.509 \times 10^{-5}$ recip. ohm
Conductivity of water (solvent).....	0.103
Conductivity of acid (solute) .....	$\frac{3.406 \times 10^{-5}}{}$ „ ( $= k_0$ )
(Hence $k_0/m_0 = 336.0$ ,	$\sqrt{m_0} = 0.0466$ .)



I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Number of solution.	Initial concentration (gramme-equivalent per litre).	Total change in quantity of $H_2SO_4$ (gramme-equivalent).			Gramme-equivalent of hydrogen liberated at cathode.	Migration constant (from Columns V and VI).	Weighted mean.
		Anode.	Cathode.	Mean.			
1	$1.0465 \times 10^{-1}$	$4.47 \times 10^{-4}$	$4.67 \times 10^{-4}$	$4.57 \times 10^{-4}$	$2.485 \times 10^{-3}$	0.184	
2	$1.0465 \times 10^{-1}$	$5.71 \times 10^{-4}$	$5.83 \times 10^{-4}$	$5.77 \times 10^{-4}$	$3.079 \times 10^{-3}$	0.187	
3	$1.0070 \times 10^{-2}$	$5.82 \times 10^{-5}$	$6.14 \times 10^{-5}$	$5.98 \times 10^{-5}$	$3.214 \times 10^{-4}$	0.186	0.186
4	$1.0070 \times 10^{-2}$	$8.65 \times 10^{-5}$	$8.96 \times 10^{-5}$	$8.80 \times 10^{-5}$	$4.744 \times 10^{-4}$	0.1855	
5	$1.0230 \times 10^{-3}$	$5.50 \times 10^{-6}$	$5.71 \times 10^{-6}$	$5.60 \times 10^{-6}$	$2.71 \times 10^{-5}$	0.206	0.186
6	$1.0230 \times 10^{-3}$	$5.49 \times 10^{-6}$	$5.64 \times 10^{-6}$	$5.56 \times 10^{-6}$	$2.96 \times 10^{-5}$	0.188	
7	$1.0255 \times 10^{-3}$	$5.49 \times 10^{-6}$	$5.51 \times 10^{-6}$	$5.50 \times 10^{-6}$	$2.93 \times 10^{-5}$	0.188	
8	$1.0255 \times 10^{-3}$	$4.09 \times 10^{-6}$	$4.13 \times 10^{-6}$	$4.11 \times 10^{-6}$	$2.18 \times 10^{-5}$	0.193	
9	$1.0165 \times 10^{-3}$	$3.37 \times 10^{-6}$	$3.49 \times 10^{-6}$	$3.43 \times 10^{-6}$	$1.864 \times 10^{-5}$	0.184	
10	$1.0165 \times 10^{-3}$	$3.52 \times 10^{-6}$	$3.48 \times 10^{-6}$	$3.50 \times 10^{-6}$	$1.864 \times 10^{-5}$	0.188	
11	$1.0165 \times 10^{-3}$	$3.90 \times 10^{-6}$	$3.92 \times 10^{-6}$	$3.91 \times 10^{-6}$	$2.11 \times 10^{-5}$	0.185	
12	$0.5133 \times 10^{-3}$	$2.57 \times 10^{-6}$	$2.59 \times 10^{-6}$	$2.58 \times 10^{-6}$	$1.402 \times 10^{-5}$	0.184	0.189
13	$0.5133 \times 10^{-3}$	$3.77 \times 10^{-6}$	$3.83 \times 10^{-6}$	$3.80 \times 10^{-6}$	$2.06 \times 10^{-5}$	0.185	
14	$0.5081 \times 10^{-3}$	$2.89 \times 10^{-6}$	$3.02 \times 10^{-6}$	$2.955 \times 10^{-6}$	$1.582 \times 10^{-5}$	0.187	
15	$0.20785 \times 10^{-3}$	$0.644 \times 10^{-6}$	$0.596 \times 10^{-6}$	$0.620 \times 10^{-6}$	$3.40 \times 10^{-6}$	0.182	0.185
16	$0.20785 \times 10^{-3}$	$1.008 \times 10^{-6}$	$0.963 \times 10^{-6}$	$0.985 \times 10^{-6}$	$5.25 \times 10^{-6}$	0.188	
17	$0.20785 \times 10^{-3}$	$1.100 \times 10^{-6}$	$1.022 \times 10^{-6}$	$1.061 \times 10^{-6}$	$5.70 \times 10^{-6}$	0.184	
18	$1.0140 \times 10^{-4}$	$5.765 \times 10^{-7}$	$5.625 \times 10^{-7}$	$5.695 \times 10^{-7}$	$2.93 \times 10^{-6}$	0.195	0.1855
19	$1.0140 \times 10^{-4}$	$5.15 \times 10^{-7}$	$5.18 \times 10^{-7}$	$5.165 \times 10^{-7}$	$2.69 \times 10^{-6}$	0.192	
20	$1.0140 \times 10^{-4}$	$6.65 \times 10^{-7}$	$6.55 \times 10^{-7}$	$6.60 \times 10^{-7}$	$3.38 \times 10^{-6}$	0.195	
21	$0.5440 \times 10^{-4}$	$3.18 \times 10^{-7}$	$3.25 \times 10^{-7}$	$3.215 \times 10^{-7}$	$1.566 \times 10^{-6}$	0.206	0.194
22	$0.5440 \times 10^{-4}$	$3.78 \times 10^{-7}$	$3.78 \times 10^{-7}$	$3.78 \times 10^{-7}$	$1.827 \times 10^{-6}$	0.207	
23	$0.5405 \times 10^{-4}$	$2.83 \times 10^{-7}$	$2.83 \times 10^{-7}$	$2.83 \times 10^{-7}$	$1.392 \times 10^{-6}$	0.203	
24	$0.5405 \times 10^{-4}$	$3.01 \times 10^{-7}$	$3.08 \times 10^{-7}$	$3.045 \times 10^{-7}$	$1.522 \times 10^{-6}$	0.200	
25	$0.5832 \times 10^{-4}$	$2.62 \times 10^{-7}$	$2.56 \times 10^{-7}$	$2.59 \times 10^{-7}$	$1.359 \times 10^{-6}$	0.191	
26	$0.5832 \times 10^{-4}$	$5.58 \times 10^{-7}$	$5.50 \times 10^{-7}$	$5.54 \times 10^{-7}$	$2.756 \times 10^{-6}$	0.201	
							0.202

be transferred to the conductivity cell, and for which the discrepancies between the changes on the two sides were rather large, the value obtained for the migration constant is not very trustworthy. Of the three experiments performed with this solution, that showing the best agreement between the

measured changes at the anode and cathode is the one giving 0.188 as the migration constant.

It was found that the conductivities of solutions of the same strength made up with different specimens of distilled water were not the same. When the discrepancy was small, the procedure adopted in calculation was as follows. From the conductivity of the solution a value for the concentration was calculated from the curve which had been already drawn. Let  $m$  be this value, and  $m_0$  the true concentration. Then, from the standpoint of the conductivity curve,  $m_0$  gramme-equivalents behave as though they were  $m$  gramme-equivalents. Hence, concentrations deduced from the curve were multiplied by the factor  $m_0/m$  to get the true concentrations. We get practically the same result, if, calculating  $k/m_0$  for the solution, we increase or decrease the ordinates of the curve (by some fixed length) until it passes through the point showing the true value of  $k/m$  for the solution, and calculate concentrations from this curve. The corrections made in this way were only small ones, so that, though the method of correcting has no very firm theoretical basis, it is probably accurate enough for the purpose.

In the case of one or two of the weakest solutions made up six or seven weeks after the rest of the experiments had been performed, the discrepancy was rather large. For these solutions fresh conductivity curves were plotted (from direct experiment) which passed very near the points corresponding to the new solutions, and from these curves the "final concentrations" were calculated for these solutions.

It will be noticed that some of the values for the transport ratio are abnormally divergent from the mean. There was nothing in the course of these particular experiments to lead one to regard the results as untrustworthy. An explanation of the divergence will be suggested later. In deducing the "mean" of the results of individual experiments, however, no account was taken of this explanation; the final results, therefore, are purely experimental.

### 5. *Theoretical Considerations.*

These experiments seem to show an increase in the migration constant at extreme dilutions. If this be due to the falling-off in velocity of the hydrogen ion, we can calculate what the rise in the migration constant should be in order to account for the drop in the equivalent conductivity curve. To do this, it is necessary to make some assumption as to the cause of the smaller velocity of the hydrogen ion, and so deduce what the conductivity would have been if the velocity had remained unaltered. It has long been noticed that the phenomenon under investigation is observed

only for acids and alkalies, *i.e.*, those substances which in solution form hydrogen or hydroxyl ions, the ions of the solvent. Considerations of mass action show at once that the ionisation of the water is greatly reduced by the presence of a trace of acid or alkali. The greater the concentration of the acid, the smaller will be the ionisation of the water. Assuming that the conductivity of Kohlrausch's purest water ( $0.87 \times 10^{-7}$ ) gives us approximately a measure of its ionisation in these conditions, it may be shown that for concentrations of acid or alkali greater than  $10^{-7}$  gramme-equivalent per litre, the number of hydroxyl or hydrogen ions from the water is inversely proportional to the quantity of acid or alkali in solution.

If the diminution in the equivalent conductivity of acid solutions at extreme dilutions be caused by the water itself rather than by impurities, it is reasonable to suppose that the effect would be directly proportional to the ionisation of the water, and hence inversely proportional to the concentration of the acid, the effect becoming greater as the dilution proceeds. Now, if at points along the equivalent conductivity ( $k/m$ ) curve we add ordinates proportional to the concentration of the hydroxyl ions (*i.e.*, inversely proportional to the concentration of the acid), we obtain another curve. For one particular proportionality, and one only, this curve gradually becomes horizontal as it approaches the axis for zero concentration; that is, it neither dips nor rises. If the proportionality be greater than this critical value, the curve would rise more and more rapidly, while if a smaller proportionality be taken, the curve would descend (in a manner similar to the actual experimental curve). It seems feasible, as a working hypothesis, to regard the critical curve so obtained as giving us the  $k/m$  curve which would have indicated the conductivity, had the ionisation of the water remained unaltered.

We can now calculate the change in the migration constant which results from the diminution in conductivity—assuming that diminution to be due to the decrease in velocity of one of the ions.

Let  $u$  and  $v$  be the velocities of the anion and cation respectively,  $u$  being variable. Then at any particular concentration, the conductivity  $k$  of the acid is equal to  $c(u+v)$ , where  $c$  is a constant. The transport ratio  $\mu$  for the anion is equal to  $v/(u+v)$ . Thus  $\mu k$  is equal to  $cv$ , and is therefore constant.

Let  $\mu_1$  and  $k_1$  refer to the experimental curve, and  $\mu_2$  and  $k_2$  to the theoretical one. We regard  $\mu_2$  as remaining constant. Its numerical value is obtained from experiments on solutions for which  $k_1$  and  $k_2$  are practically equal, for then  $\mu_2 = \mu_1$ . For any particular concentration we now have  $k_1$ ,  $k_2$ , and  $\mu_2$ ; hence  $\mu_1$ , the actual migration constant, is obtained.



The process described above of plotting the theoretical curve was carried out with the  $k/m$  curve given in the paper already referred to.\* Since certain impurities have a considerable effect in lowering the conductivity, it seemed feasible to take the highest curve which consistently resulted from experiment, and regard the lowness of others as being due to impurities.

The following values were then obtained, the value of  $\mu_2$  being taken as 0.186.

Concentration (gramme-equiv. per litre).	$k_2$ (theoretical).	$k_1$ (experimental).	$u_1 = \frac{k_2}{k_1} u_2$
0.001	367	365	0.187
0.0005	378	374.5	0.1875
0.0002	387	378.5	0.190
0.0001	399	378.5	0.1935
0.00005	390	358.5	0.2025
0.00003	390.5	339.5	0.214

The "theoretical" migration curve, plotted from the figures in the last column of this table, is shown in the following diagram as a smooth line, and the experimental values obtained (Column VIII of table in § 4) are indicated by crosses.

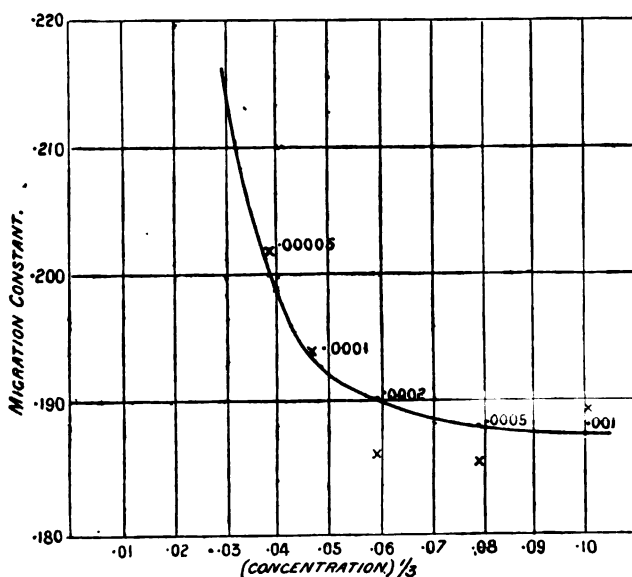


FIG. 4.

\* Whetham, 'Roy. Soc. Proc.' A, vol. 76, p, 582, 1905.

§ 6. It was thought at first that these experiments gave fresh evidence in favour of the theory that the velocity of the hydrogen ion is diminished at extreme dilution, and that this diminution accounts for the drop in the  $k/m$  curve. The extent of the change observed in the migration constant seemed strongly to favour this explanation. Further examination, however, including a calculation of the effect of impurities, shows that the theory receives no support from these experiments, the whole of the rise attributed to the migration constant being readily accounted for when we take into consideration the residual conductivity of the water. Let us, then, consider the problem from the standpoint of a supposed unaltered migration constant.

Let us imagine the conductivity of the distilled water to be due to the presence of some substance AB which becomes ionised in the solution. For all the substances likely to constitute this impurity, hydrogen will be evolved at the cathode, and oxygen at the anode, when the solution is electrolysed. As in the electrolysis of sulphuric acid, the total quantity of solute will remain constant, and the change at the anode will be balanced exactly by that at the cathode. Consider a solution of sulphuric acid containing  $m$  gramme-equivalents of the acid per cubic centimetre, and let there be, in this solution,  $n$  gramme-equivalents of the substance AB in the ionised state.

Let  $u$  be the velocity of the H ion,  $v$  of the  $(\text{SO}_4)$  ion,  $u'$  of the A ion,  $v'$  of the B ion; we have  $u = 319$ ,  $v = 73$ , as deduced from the "limiting" equivalent conductivity and the migration constant of sulphuric acid.

The conductivity of the solution is  $m(u+v) + n(u'+v) = K$ , say. Suppose 1 gramme-equivalent of hydrogen to be liberated at the cathode. Distributing the conductivity amongst the several ions, we deduce the following changes in the anode region:—

$mv/K$  grm.-equiv. of  $\text{SO}_4$  ions enters;  $nv'/K$  grm.-equiv. of B ions enters;  
 $mu/K$  grm.-equiv. of H ions leaves;  $nu'/K$  grm.-equiv. of A ions leaves.

Also by the action on the water of the  $\text{SO}_4$  and B ions, liberated at the anode, 1 gramme-equivalent of H ions are formed. Hence, in the anode region, there is a net gain of H ions amounting to  $\{mv + n(u' + v')\}/K$  gramme-equivalent.

Hence the total conductivity of the solution at the anode is increased by the amount

$$[mv \cdot v + nv' \cdot v' + \{mv + n(u' + v')\}u - nu' \cdot u']/K,$$

which is  $\{mv(u+v) + n(u'+v')(u+v'-u')\}/K$ .

If instead of drawing the "equivalent conductivity" curve in the usual way, we plot the specific conductivity ( $k$ ) against the concentration ( $m$ ), we shall find that the curve so drawn is a straight line (not passing through the

origin). Hence the increase in conductivity is interpreted as being directly proportional to the increase in the concentration, and consequently (for equal quantities of hydrogen evolved at the cathode) directly proportional to the migration constant, as measured in these experiments.

For pure water and sulphuric acid,  $n = 0$ , and the increase in the conductivity becomes  $mv(u+v)/m(u+v) = v = 73$ .

The conductivity of the water used was about  $10^{-6}$ . Let us regard this for the moment as being wholly due to the impurity present. For acid substances, like carbonic acid, which are only slightly ionised and have an ion in common with sulphuric acid, this number must be reduced to indicate the conductivity of AB in the acid solution, as the presence of the sulphuric acid diminishes the ionisation of carbonic acid. For the corresponding saline substances (sulphates) the suppression would be inappreciable.

1. If the impurity be free acid, we have  $u = u'$ , and the above expression reduces to  $\{mv(u+v) + nv'(u+v')\}/K$ . For the weakest solutions of sulphuric acid used, the conductivity was  $18 \times 10^{-6}$ , so that

$$m(u+v) = 18 \times 10^{-6}, \quad n(u+v') = 1 \times 10^{-6}.$$

Hence the expression for the increase in conductivity becomes

$$(18v+v') \times 10^{-6} / 19 \times 10^{-6},$$

which is never much greater than  $v$ , since there are no anions (with the exception of the hydroxyl ion) which have a velocity appreciably greater than that of the sulphate ion. Hence the increase in conductivity at the anode, and the decrease at the cathode, is never appreciably greater than it is when no such impurity is present. With ions for which  $v' < v$ , the migration constant would appear to be diminished. The extreme effect for the above concentrations of sulphuric acid would be 1 part in 19 (*i.e.*,  $v' = 0$ ), reducing the measured value of the migration constant from 0.186 to 0.176. For any real ions, however,  $v'$  is never less than about 40, so that the migration constant would never appear to be less than about 0.182. For very weak acids (*e.g.*, carbonic acid) all such effects are very much reduced, as their "partial conductivity" would be much less than  $10^{-6}$  in the presence of the sulphuric acid. We may conclude, therefore, that the presence of acid impurities in the water used as solvent cannot explain the large increase observed in the migration constant.

2. If the impurity in the water consisted of free alkali, it would be neutralised by the acid, the hydroxyl and hydrogen ions disappearing from solution. We shall find that, though the presence of traces of salt, such as potassium chloride, has no effect on the partial conductivity of the acid, yet it has a very pronounced effect upon the transport ratio as measured in the previously described experiments.

As before, we have the formula for the increase in conductivity at the anode,

$$\{mv(u+v) + n(u'+v')(u+v'-u')\}/K.$$

Since  $u$  ( $= 319$ ) would always be large compared with  $(v'-u')$ , we may get an approximate value for this expression, writing it

$$\{mv(u+v) + nu(u'+v')\}/K.$$

Since H and (OH) ions are excepted,  $v'$  and  $u'$ , even in extreme cases, would never differ by more than 30, and hence the maximum error we introduce by taking this approximation is about 1 in 50, thereby making the transport ratio uncertain to the extent of three or four units in the third decimal place. On the theory to be suggested later, there is practically no difference between  $v'$  and  $u'$ , so that the approximation is nearly exact. Putting in the values as before, we get  $\{18 \times 10^{-6} \times 73 + 319 \times 10^{-6}\} / \{18 \times 10^{-6} + 10^{-6}\} = 86$ . Hence for a solution of this strength, the migration constant appears to be increased in the ratio 86/73, i.e., from 0.186 to 0.219.

This rise is greater than that actually observed. Hence, to explain the experimental results, it is only necessary to assume that about half the conductivity of the water used is due to (alkaline or) saline impurity. That such impurity should be present is more than likely; if present, its effect as described above is certain.

The physical explanation of the result of the above analysis is as follows. If the conductivity of the water ( $10^{-6}$ ) were due to the presence of sulphuric acid, the migration constant would be unaffected. When the ion A replaces the hydrogen ion, a much larger number of molecules (between three and four times as many) is required to make up the initial conductivity,  $10^{-6}$ . Hence, in the migration, between three and four times as many B ions enter the anode region as before. Since the increase in conductivity of the solution at the anode is nearly proportional to the number of  $\text{SO}_4$  and B ions entering the region, and since the proportion of B ions to  $\text{SO}_4$  ions for these concentrations of sulphuric acid is quite appreciable, and the velocities of the two ions of the same order, it follows that we should expect a marked effect on the change in conductivity from which the migration constant is deduced.

§ 7. The experimental results obtained, therefore, give no evidence in favour of the rise in the true migration constant of sulphuric acid at extreme dilutions; the whole of the apparent rise can be explained logically in a more simple way. In fact, these experiments point rather to a constant value for the transport ratio, though they would not be inconsistent with a gradual decrease in that ratio.

The above analysis also explains why the results for individual experiments

sometimes varied rather widely from the mean: the supposition that a slight variation in the amount of impurity occurred, owing to the absorption of ammonia from the air, for example, being sufficient for the purpose. Also, it was noticed throughout the research, though the fact had to be left unexplained at the time, that experiments performed with different portions of the same prepared solution generally gave results which agreed better amongst themselves than with those deduced from the use of other specimens of solution of practically the same strength. That still greater irregularity was not shown is accounted for by the fact that the various specimens of distilled water were always prepared in similar conditions, and the conductivity never varied more than 1 part in 20 from the average.

#### 8. *The Conductivity Curve.*

We are thus led to consider once more the cause of the drop in the equivalent conductivity curve. The evidence seems conclusive against the supposition that the presence of carbonic acid, or indeed of any other acid, is sufficient to explain the phenomenon.

In the same series of experiments as those with exhausted water, referred to in the first part of the paper, the effect of the presence of carbonic acid deliberately introduced into the solution was ascertained.\* If instead of plotting the  $k/m$  curve as was there done, we plot the total conductivity of the solution against the concentration of sulphuric acid—both for the solution containing carbonic acid, and that made up from the pure distilled water—we shall find that the curve for the former case always lies above that for the latter, the two gradually merging as the concentration increases. The difference between the ordinates of the two curves at any particular concentration gives us the effect of the carbonic acid on the conductivity. The effect is always positive, but diminishes in magnitude as the concentration of the sulphuric acid increases. This is explained simply and logically on the supposition that the carbonic acid behaves as a “second acid,” contributing its partial conductivity to the whole conductivity of the solution. Since it is a very weak acid, its ionisation is suppressed by the hydrogen ions of the sulphuric acid, and hence its effect will become less and less, ultimately becoming negligible, as the concentration of the sulphuric acid increases. Hence, by subtracting the full initial conductivity of the solvent containing carbonic acid, we make the partial conductivity of the sulphuric acid appear smaller than it really is, and thus apparently get a drop in the  $k/m$  curve. If the purest distilled water contained carbonic acid, the presence of this

\* ‘Roy. Soc. Proc.’ A, vol. 76, p. 580.

impurity would explain part of the drop observed, but there remains an excess effect to be accounted for in another way.

For let us consider the equivalent conductivity curve for a solution made up with the purest water obtained by distillation in air. If, instead of deducting the conductivity of the solvent, we take the total conductivity of the solution in plotting the  $k/m$  curve, we shall find that the curve still falls off at extreme dilutions. Since the effect of carbonic acid is always additive, correcting for it, to get the true conductivity of the sulphuric acid, can only exaggerate the drop in this curve. Hence, on the basis of any known phenomenon, the presence of carbonic acid, or of any other free acid, is insufficient to explain the whole of the apparent diminution in the conductivity of the sulphuric acid.

Water distilled *in vacuo* has a much smaller conductivity than that distilled in air; hence most of the impurities in the latter are dissolved from the air. Now the atmospheric gases most likely to be dissolved in any appreciable quantity are carbonic acid and ammonia. Normally there is forty times as much carbonic acid as ammonia in the atmosphere, but the solubility of ammonia is so much greater than that of carbonic acid that the quantities of each which would be present in solution are probably of one and the same order.

Let us, then, regard the solvent as containing ammonium carbonate, which at such dilution would be largely in the ionised state. The addition of a strong acid will result in the formation of un-ionised carbonic acid—the ammonium ions remaining in solution. Some of the hydrogen ions of the strong acid have thus been removed. We may regard the first small quantity of acid added as being removed from the solution or rendered inactive, and the partial conductivity as due to the portion left.

Again, instead of adding an acid, let us introduce a strong alkali like potash. Here we shall have un-ionised ammonia (or ammonium hydrate) formed, and some of the hydroxyl ions of the strong alkali will be removed from the solution. As before, the effect is the same as though the first portion of alkali added had been nullified.

This view is best made evident from the conductivity curve—plotting the “partial conductivity” of the acid (the conductivity of the solution minus the initial conductivity of the solvent) against the mass of acid added. A quantitative as well as a qualitative agreement with facts may be observed. The curve is a straight line. When produced it does not pass through the origin, but cuts the axis of zero conductivity at a point showing the concentration of acid to be  $4.7 \times 10^{-6}$  gramme-equivalent per litre (for a curve plotted during the course of the experiments described in this paper). The

effect on the conductivity therefore is the same as though this quantity of acid had been neutralised or removed from solution. Now from the migration constant experiments, since the rise in the measured migration constant was only half what we should expect if the whole of the conductivity of the solvent had been due to saline matter, we may conclude that about half this quantity of salt was present in the water, giving a conductivity of about  $5 \times 10^{-7}$ . Suppose this salt to be ammonium carbonate. The velocity of the  $\text{CO}_3$  ion (deduced from the migration constants of potassium and sodium carbonates and sulphates) is about 50, while that of the  $(\text{NH}_4)$  ion (deduced in a similar manner from the figures for ammonium chloride, etc.) is about 70. Hence  $u + v = 120$ . We then get  $k = m(u + v) = 5 \times 10^{-7}$ , so that  $m = 5 \times 10^{-7}/120 = 4.2 \times 10^{-9}$  gramme-equivalent per cubic centimetre, or  $4.2 \times 10^{-6}$  gramme-equivalent per litre.

If this be the quantity of ammonium carbonate present in solution, it would account for the neutralisation of an equivalent quantity of sulphuric acid. The agreement with the number deduced from the conductivity curve is very close indeed.

It was also noticed that, when exposed to the air, the conductivities of dilute solutions of acid diminished, often at a considerable rate. That no solution of alkali from the glass produced this effect was shown by preventing the air from getting into contact with the solution, when the conductivity remained quite constant. This seems to show that ammonia, or some other alkali, is readily absorbed from the atmosphere—the hydrogen ions being replaced by ammonium ions in the solution, and the total conductivity being diminished.

There is an objection which must be faced. A solution of ammonium carbonate, on boiling, gives off ammonia and carbonic acid. Hence, in the exhaustion experiments described in the first part of this paper, when the conductivity of the solvent was considerably reduced before the addition of the sulphuric acid, we might have expected that some of the ammonium carbonate would have been abstracted, and the effect made apparent on the  $k/m$  curve. It must be remembered, however, that the last traces of ammonia would be removed only with great difficulty. Further, from the above calculations it would appear probable that half the conductivity of the solvent is due to the presence of something which does not affect the transport ratio. If this represents an excess of carbonic acid, the results are explained. Since ammonia is much more soluble than carbonic acid, the latter would be evolved much more readily on exhausting the water. Hence the diminution in conductivity would be accounted for by the removal of the carbonic acid, while the ammonia present may be almost unaffected.

9. We have sought to explain the apparent diminution in the equivalent conductivity of acids (and similarly of alkalies) at extreme dilution by the association of ions brought together in solution. Such an association would take place if the solvent contained: (1) a weak acid such as carbonic acid, (2) a weak alkali such as ammonia, or (3) a salt formed by the neutralisation of a weak acid by a weak alkali, such as ammonium carbonate. We have seen that experimental evidence is opposed to the supposition that the presence of carbonic acid alone is sufficient to explain the phenomenon; we have concluded that the presence of ammonium carbonate is capable of providing this explanation. It has been shown that the diminution in the equivalent conductivity would be accounted for if by some means the conductivity of  $4.7 \times 10^{-6}$  gramme-equivalent of sulphuric acid per litre were destroyed. Hence the "impurity" in the water must be such as will produce this electrical effect. Now consider the three cases. In the first, we should get approximately the same result electrically, if there were  $5 \times 10^{-6}$  gramme-equivalent of ionised carbonic acid per litre of the solvent, which becomes un-ionised on the addition of the strong acid; in the second,  $3.5 \times 10^{-6}$  gramme-equivalent of ionised ammonia per litre would be sufficient; and in the third,  $5 \times 10^{-6}$  gramme-equivalent per litre of ammonium carbonate—also in the ionised state. The conductivities of these solutions would be

$$\begin{aligned} (1) \quad k_1 &= 5 \times 10^{-9} (319 + 50) = 1.8 \times 10^{-6}, \\ (2) \quad k_2 &= 3.5 \times 10^{-9} (184 + 70) = 0.9 \times 10^{-6}, \\ (3) \quad k_3 &= 5 \times 10^{-9} (70 + 50) = 0.6 \times 10^{-6}. \end{aligned}$$

The actual conductivity of the water was between  $0.9 \times 10^{-6}$  and  $1.0 \times 10^{-6}$ . Hence there could not have been sufficient carbonic acid present in the free state in the distilled water to account for the observed "diminution" in the conductivity of the solution. The conductivity of the water easily allows for the presence of sufficient ammonium carbonate. The case for ammonia is just on the border line. The high velocities of the hydrogen and hydroxyl ions make the number of gramme-equivalents of an acid or alkali required to produce a given conductivity less than that of a salt. That is why, for a given conductivity, ammonium carbonate is more effective in reducing the conductivity of the solution of sulphuric acid than ammonia or carbonic acid present separately.

We have assumed throughout this final investigation that the velocities of the ions remain constant for the greatest dilutions. It is still possible that these velocities diminish, and that the above explanation only partially accounts for the drop in the  $k/m$  curve. To complete the solution of the



problem, it would be necessary, either to obtain an exact knowledge of the impurities in the water, so as to allow for their effect, or to use water which contained no such impurities. In the water distilled in air it is probable that ammonia and carbonic acid are dissolved; if so, the effect in diminishing the conductivity necessarily follows.

*Studies of the Processes operative in Solutions.*—Parts VI—X.

By Professor H. E. ARMSTRONG, F.R.S. and others.

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[*International Catalogue of Scientific Literature.*

Authors' title slips :—C D VI—X.

- VI D 7050 Title.
- D 7175 Nature of the process of dissolution.
- D 7275 } Explanation of electrolytic conductivity.
- C 6250 }
- D 7090 (Hydrolysis) Title.
- D 7090 (Neutralisation) Interaction of acids and alkalies explained on association hypothesis.
- D 7260 The ionic association hypothesis.
- D 7170 Viscosity, explanation of.
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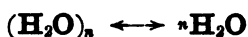
VI.\* *Hydrolysis, Hydration and Hydratation as Determinants of the Properties of Aqueous Solutions.* By H. E. ARMSTRONG, F.R.S.

In this communication I desire to take a definite step towards an explanation of the fundamental changes attending dissolution and other operations in

\* No. I, 'Roy. Soc. Proc.,' A, vol. 78, 1906, pp. 272—295; II—V, 'Roy. Soc. Proc.,' A, vol. 79, 1907, pp. 564—597.

aqueous solutions, by contending that dissolution involves associative and distributive changes which are necessary precursors of all chemical interchanges effected in such solutions.\*

Both in my address to the Chemical Section of the British Association in 1885 and in my communication to this Society in 1886,† stress was laid on the reciprocal parts which solvent and solute play in the process of electrolysis. But I went too far in attributing, in all cases, the increase in molecular conductivity which is usually conditioned by dilution to the gradual molecular simplification (depolymerisation) of the dissolved substance. Moreover, although I contended that water plays a dominant part and called attention specially to its complex molecular structure, I but dimly perceived how great must be the influence exercised by the change effected in the composition of water itself—and the consequent alteration in its properties—when a substance is dissolved in it; the nature and *all-important* character of this influence only became apparent to me after the discussion on ionisation in Section A at the British Association at Bradford in 1900.‡ The consequences of the assumption that the dissociative change pictured in the equation



is of constant occurrence in water were somewhat more fully developed in my communication to this Society "On the Origin of Osmotic Effects."

*Nature of the Process of Dissolution.*—Although in the case of salts and not a few other substances the simplification of polymers undoubtedly plays an important part, judging from its volatility it is probable that a substance such as hydrogen chloride enters into solution in water entirely in the monadic form, as HCl: in any case, it is unlikely that molecular complexes are ever present, even in the most concentrated solutions of this hydride, in proportions sufficient to account for the considerable changes which attend the dilution of such solutions. Hydrogen fluoride and sulphuric acid, on the other hand, both exist, presumably, to some extent in the form of polymers, even in moderately dilute solutions.

A satisfactory and, I believe, complete explanation of the properties of solutions of hydrogen chloride may be given on the assumption that when it

\* Since 1885 my conviction has never varied that the hypothesis that the ions are free in solutions is one which does not and cannot afford an explanation of the facts as these present themselves to the chemist. It is only because chemical considerations have been laid aside and because the problem has been regarded from an artificial standpoint that the hypothesis has met with acceptance.

† 'B.A. Report,' 1885, p. 952; 'Roy. Soc. Proc.,' vol. 40, p. 268.

‡ 'Encyclopædia Britannica,' 1902, vol. 26, p. 741.

is dissolved in water interactions take place which involve the production of the following complexes:—



Definite expression is here given to the manner in which the “residual affinity” of the negative elements is exercised on which I laid much stress in 1885 and 1886, at a time when chemists were in no way prepared to acknowledge the extent to which this force is operative in conditioning chemical change.

I regard the bipartite, composite molecules (a) and (b) as the effective molecules and propose to speak of such complex molecules as the effective molecules and of their active components as the effective radicles in a solution of hydrogen chloride; being closed systems, molecules of the type  $\text{H}_2\text{O} : \text{ClH}$  are inactive so long as they remain unmodified.

I avoid the terms ion, ionised and ionisation advisedly, as these now have an ambiguous meaning.

In the process pictured, the dissolved substance is in part hydrolysed, the component radicles being rearranged—but *not set free*; at the same time, the simple molecules contained in water also undergo scission and their component radicles are, in like manner, rearranged—but *not set free*. *I regard this double effect of admixture as a necessary step in the formation of a composite electrolyte.*

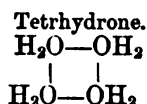
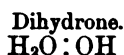
In cases in which only the molecules of the solvent undergo resolution, the solution obtained is not an electrolyte; in other words, composite hydrols of the type  $\text{RX} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$  when alone are not electrolytes.

This explanation of the process of dissolution is, I venture to think, generally applicable.

To consider the changes somewhat more in detail. Water itself, it is to be supposed, is a complex mixture of active and inactive molecules;\* the active molecules being either simple monad-hydrone ( $\text{OH}_2$ ) molecules or hydrone-hydrol (briefly, hydronol) molecules ( $\text{H}_2\text{O} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$ ); the inactive, the closed

\* *Nomenclature.*—In order that a proper distinction may be made between the molecules in water which are to be regarded as active and the admixture of these with various inactive polymers which constitutes liquid water, I propose to confine the term *Water* to the admixture. It is inadvisable, I think, to follow Sutherland in speaking of the simple molecule of water as Hydrol, especially as this term was applied by me in 1880 to the unstable hydroxy-derivatives formed by the combination of the elements of water with aldehydes and acids (aldehydrols and acidhydrols). The *ol* terminal is now used strictly by chemists, as significant of the alcoholic function. Water belongs rather to the ketonic class—to the *ones*: the simple molecule  $\text{H}_2\text{O}$  may therefore be termed *Hydrone*; the term Hydrol may be reserved for use in reference to compounds in which the constituent radicles of hydrone function separately.

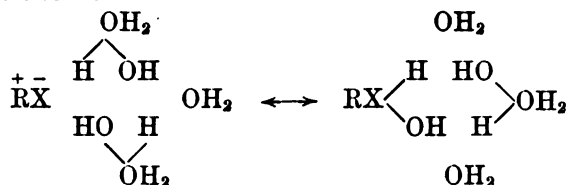
systems which are formed by the *association* unaccompanied by *distribution* of two or more simple molecules—such as are represented by the formulæ:—



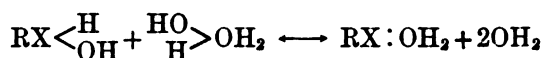
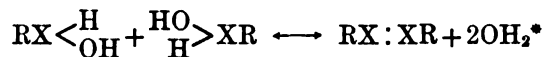
Whether or no all these modifications would arise in the entire absence of other substances is uncertain. Bearing in mind that it is possible both to super-cool and super-heat water in the absence of appropriate equilibrators, it is difficult to say what the behaviour of *pure* water would be: such a substance is and must ever remain an abstraction; under all ordinary conditions there must always be more than sufficient impurity present to determine the interaction of the various molecules.

Regarding the problem from the standpoint of Faraday's electrolytic studies, and in view of the well-known observations of De la Rive, Brereton Baker, Cowper and Dixon, I assume, however, that no two molecules can interact directly: that in all cases of chemical interchange (including electrolysis) the necessary *slope of potential* can only be provided by the inclusion of the interacting substances in a triple or tripartite conducting system.

It is probable that when non-electrolytes are dissolved in water they become modified in two ways. The primary change is determined, I assume by the hydrol molecules present in the liquid, the necessary slope of potential being provided, it may be supposed, by the interposition of an active hydrone molecule in the circuit.



The solution thus obtained is not an electrolyte, but contains the active complex  $\text{RX} \begin{array}{c} \text{H} \\ \diagdown \quad \diagup \\ \text{OH} \end{array}$ , the activity of which is conditioned by the *distributed* hydrol. Polymerides of the compound RX are formed by the interaction of these complexes; and they may be converted by the agency of hydrol into inactive isomerides in which the hydrone is associated with the compound RX, but not distributed.



\* In this and subsequent equations no attempt is made to indicate the nature of the "circuit" or system within which the interchange occurs.

In the case of substances which give rise to composite electrolytes when dissolved in water, I assume that not only is the compound hydrolated, but that its simple molecules also undergo distribution, so that the solution contains the isodynamic active complexes represented by the formulæ :—



It is to be supposed that the occurrence of electrolysis in such solutions is dependent on influences which the composite molecules exercise reciprocally upon one another whilst under the influence of the electric strain.

*Electrolytic Conductivity.*—The apparent increase in the electrolytic activity of a dissolved substance on dilution is presumably due to an increase in the proportion of effective composite molecules. Such increase is ascribable to the diminution in the activity of the solvent water which is conditioned by the increase in its relative amount. Water, in fact, must be regarded as most active when present in smallest amount, as it is then present mainly in the monadic form or in association as *hydrol*, change taking place more and more completely in the direction  $(OH_2)_n \rightarrow nOH_2$  the greater the admixture of foreign substance. The withdrawal of hydrol from the effective composite molecules through the agency of the hydrol in the solvent water will therefore tend to a minimum when the solution is diluted, as the proportion of monads and of hydronol in the water becomes less and less.

In a solution of hydrogen chloride, for example, the existence of molecules of the type  $HCl < \begin{smallmatrix} OH \\ H \end{smallmatrix}$  should be favoured in weaker solutions, as in these the solvent water will have less tendency to withdraw hydrol from the complex; on the other hand, in concentrated solutions, the proportion of effective molecules of the type  $H_2O < \begin{smallmatrix} Cl \\ H \end{smallmatrix}$  should be larger than in weak solutions, as the hydrol should have greater hydrolysing efficiency in such solutions.

From this argument it follows that conductivity in concentrated solutions is conditioned mainly by molecules of the *hydrolysed* solute of the type  $H_2O < \begin{smallmatrix} H \\ Cl \end{smallmatrix}$ , whilst in weak solutions it is conditioned mainly by molecules of the *hydrolated* solute, e.g.,  $HCl < \begin{smallmatrix} H \\ OH \end{smallmatrix}$ ; in other words, the solute is mainly active as hydrolyte in concentrated solutions, the solvent in weak solutions; and their respective molecular conductivity values must lie at opposite ends of the scale of concentration—supposing, that is to say, that it be possible to distinguish their separate effects.

The conventional conception of molecular conductivity, in fact, appears to

be based on a misconception;\* and the same may be said of so-called ionic velocities. Hitherto only the negative ion derived from the solute has been taken into account, but that derived from the water present as hydrol must also be considered; when this is done and the sum of the two effects is allowed for, it will doubtless be found necessary to abandon the conception that the opposite ions of an electrolyte move at different rates. The conductivity values at extremely low dilutions are presumably in the main "hydrol" values; the reason why dilute solutions are so regular in their behaviour, however tested, is probably because in such cases the behaviour of the hydrol almost alone comes under consideration.

In discussing the problem of electrolysis in 1885 I drew attention to the current belief that when aqueous solutions are submitted to electrolysis the dissolved substance, not the water, is the actual electrolyte. It appears at least doubtful, I then said, whether this view can be justified by reference to known facts; and, after speaking of the special case of sulphuric acid, I added, "are not perhaps both (the acid and the water) affected according to the proportions in which they are present? The marked variation in the extent to which the negative ion is transferred to the positive pole, as observed by Hittorf, when solutions of different degrees of concentration are electrolysed would appear to support this view. The difference in the products, according as dilute or very concentrated solutions of sulphuric acid are used, may also be cited as an argument that the chemical changes vary with the concentration." I further pointed out that, in the event of such a view prevailing, it would be necessary to teach that the changes involved in the interaction of metals and acids were no less complex.†

In the meantime, McLeod's observations (1886)‡ on the electrolysis of solutions of sulphuric acid of different degrees of concentration and those of Haber and Grinberg§ (1898) on solutions of chlorhydric acid have shown that great differences are conditioned by concentration—differences which cannot well be explained except on the assumption that the acid system is

\* Being a value deduced by merely multiplying the specific conductivity of a solution by the volume containing a gramme-molecular proportion of the solute, it is in no way necessarily to be associated with the dissolved substance alone. The "molecular conductivities" in a series of solutions are nothing more, in fact, than a series of numbers relating to solutions of comparable equivalent strength, expressing their relative specific activities as conductors.

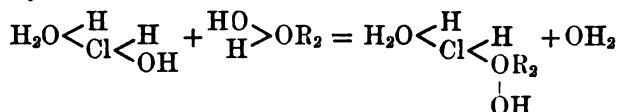
† Doumer has recently brought forward as novel this interpretation of the phenomena of electrolysis in the case of solutions of chlorhydric acid ('Comptes rendus,' 1908, vol. 146, p. 329; see also later papers).

‡ 'Chem. Soc. Trans.,' vol. 49, p. 591.

§ 'Zeits. anorg. Chem.,' 1898, vol. 16, pp. 198, 329.

mainly electrolysed in concentrated solutions and the isodynamic hydrolated system in weak—electrolysis being dependent in both cases on some reciprocal interaction of the two substances.

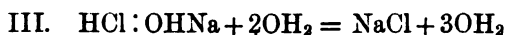
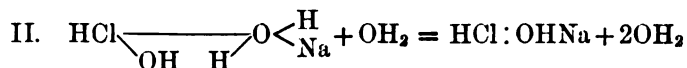
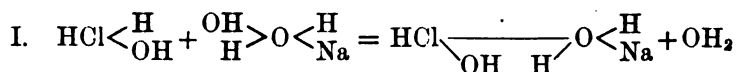
*Hydrolysis.*—Inasmuch as hydrolysis takes place the more readily the more concentrated the solution, it is to be supposed that it is conditioned by molecules of the hydrone type,  $\text{H}_2\text{O} < \begin{smallmatrix} \text{H} \\ \text{X} \end{smallmatrix}$ , not by the isomeric hydrolated complexes; moreover, that the hydrone enters into combination with the hydrolyte through the agency of the radicle X. Probably the hydrone is present in a hydrolated state, thus



Such a compound would be eminently unstable and readily break down in presence of hydrol—or in concentrated solutions under the influence of the isodynamic composites.

The behaviour of concentrated solutions of chlorhydric acid, to which reference is made in the next communication (p. 101), is in accordance with this interpretation of the character of the change.

*Interaction of Acids and Alkalies.*—The process of neutralisation may be supposed to take place in several stages, thus :—



The proportion of hydrol actually set free and the amount of water formed (I and II) will depend on the amount of associated hydrol in the effective composite molecules of acid and alkali, together with the molecular proportion liberated in the final change (III), less the amount effectively associated with the dissolved salt—at most, two molecular proportions, therefore. Inasmuch as hydrolation appears never to be complete (except sometimes in very dilute solutions) and is very far from being complete under all conditions in the case of weak acids and compounds such as ammonia, it is probable that the amount liberated, as a rule, falls considerably below two molecular proportions.

Ostwald, who has used the change in volume which attends the neutralisation of acids as a means of grading them in order of their relative affinities,

has already pointed out that the volume increase is greater than the volume of the water formed (in the final change marked III above). Thus, on mixing "kilogramme normal" solutions of nitric acid and potassic hydroxide, he observed an expansion amounting to 20.05 c.c.; but in the case of ammonia and nitric acid there was a contraction of 6.44 c.c., whilst on mixing acetic acid and ammonia the contraction amounted to as much as 16.26 c.c.

The method adopted by Ostwald of comparing solutions containing equivalent proportions of the solute *per kilogramme* is a peculiar one; when solutions are contrasted (Table I) containing comparable proportions of solute and solvent (weight-normal molecular), the results are more striking, differences becoming apparent which are not shown in Ostwald's table; thus the change in volume is considerably greater in the case of caustic soda than of potash, for example; no such difference was observed by Ostwald. It would seem that the hydroxide of sodium is more active than that of potassium, just as the sodium salts generally are more active than those of potassium.

Table I.

Vol. of weight-normal molecular solutions at 25°	KOH = 1014.68	HCl = 1021.98
	NaOH = 1001.28	HNO <sub>3</sub> = 1033.25
Water, 1000 grammes = 1002.97 c.c.		
(KOH) + (HCl) = 2036.66 - 2005.94 = 30.72 c.c.		
KCl = 1031.92 + H <sub>2</sub> O = 1049.97 - 1002.97 = 47.00 c.c.	Ostwald.	
(18.05 c.c.)	Expansion = 16.28 c.c.	19.52
NaOH + HCl = 2023.26 - 2005.94 = 17.32 c.c.		
NaCl = 1021.61 + H <sub>2</sub> O = 1039.66 - 1002.97 = 36.69 c.c.		
	Expansion = 19.37 c.c.	20.05
KOH + HNO <sub>3</sub> = 2047.93 - 2005.94 = 41.99 c.c.		
KNO <sub>3</sub> = 1043.48 + H <sub>2</sub> O = 1061.53 - 1002.97 = 58.56 c.c.		
	Expansion = 16.57 c.c.	19.24
NaOH + HNO <sub>3</sub> = 2034.53 - 2005.94 = 28.59 c.c.		
NaNO <sub>3</sub> = 1033.22 + H <sub>2</sub> O = 1051.27 - 1002.97 = 48.30 c.c.		
	Expansion = 19.71 c.c.	19.77

The difficulty of explaining such results from an ionic standpoint has never been sufficiently considered. On the assumption that when binary compounds which afford conducting solutions are dissolved in water they undergo dissociation into separate free ions, these latter must occupy less space than the substances from which they are derived, since the dissolution of such substances involves a considerable diminution in volume. But, according to this hypothesis, the neutralisation of an acid by a hydroxide merely involves the union of hydrogen ions from the acid with hydroxyl ions from the alkali, the other ions remaining unchanged—the expansion must therefore be entirely a consequence of this formation of water from free



hydrogen and free hydroxyl ions. These conclusions are scarcely such that they can be regarded as acceptable, as the increase in volume is largely in excess of the amount to be expected in the case of the stronger acids.

If, however, it be assumed that the change in volume on neutralisation is the measure of the difference between the water formed in the three ways shown above and that fixed by the resulting salt (including the changes in the state of dissociation of the water), a simple explanation is obtained applicable to ammonium salts as well as to metallic salts generally, the contraction in the case of ammonium salts being due to the fixation of the water by the salt, the amount fixed being very large in a case such as that of acetic acid in proportion to that liberated from the ammonia and the acid.

The precise character of the changes in volume which attend the dissolution of salts cannot well be determined, no means of estimating the liquid volume of the salt in solution being at our disposal. There is reason to believe that loosely held "water of hydration" has much the same volume as ordinary water. As ice has a volume so very different from that of liquid water, it is clear, however, that volume is a more or less relative matter; and if ice can exist of density 1.1, as stated by Tamman, some forms of water molecules are certainly capable of occupying considerably less space than we are in the habit of supposing.

The behaviour of non-electrolytes with water is also significant. To take the case of methylic acetate, as this is considered in the next communication, when the half of one gramme-molecular proportion (42.04 c.c.) is added to 1000 grammes of water at 25°, the volume diminishes by 5.67 c.c. or 13.5 per cent. It is scarcely probable either that the volume of the acetate changes materially on dissolution or that the acetate becomes hydrolated to any extent; consequently, the change in volume must be attributed, at all events in large measure, to an alteration in the water—to an increase in the proportion of hydrone and hydronol; and if this be the origin of the change, it follows that the volume of hydrone and of hydronol is less than that of water. In favour of this conclusion also we have the fact that the rotatory power of cane-sugar in solution is diminished in the direction of concentration by pressure (*cp.* I, p. 278) and that pressure diminishes the rate at which cane-sugar is hydrolysed (Röntgen, etc.); according to the view now advocated, the degree of hydrolation and hydronation of a substance such as sugar would be diminished by an increase of hydrol and hydrone and pressure should favour the dissociation of water into hydrol and hydrone if the latter have the smaller volume.

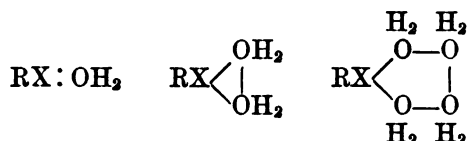
Moreover, applying considerations such as have been developed by Barlow and Pope, there is reason to suppose that considerable condensation, if not

a complete disappearance, of their volume might attend the fixation of hydrone as hydrol in the manner pictured, especially as this involves the close packing of the radicles H and OH, not of the actual hydrone molecules in the assemblage.

According to these assumptions, the changes of volume which attend dissolution, and especially those which attend dilution, apart from those arising from changes in the water, are largely, when not entirely, a consequence of constitutive changes—being mainly conditioned by the degree of effective hydration—*i.e.*, hydrolation, etc., of the molecules of the solute. As there is reason to suppose, however, that salts are only gradually resolved by dilution into the monadic form, the change in volume is not in itself a simple measure of the extent to which the molecules are rendered effective by hydrolation; the slowness with which hydrogen fluoride, for example, increases in conductivity would seem to be sufficient proof that the depolymerisation process may be a very gradual one even in the case of a volatile substance.

In concentrated solutions, active molecules of the solute presumably exercise an effect comparable with that which active molecules of the solvent produce in less concentrated and dilute solutions: in fact, the two series of effects must be regarded as operative throughout the entire range of concentrations.

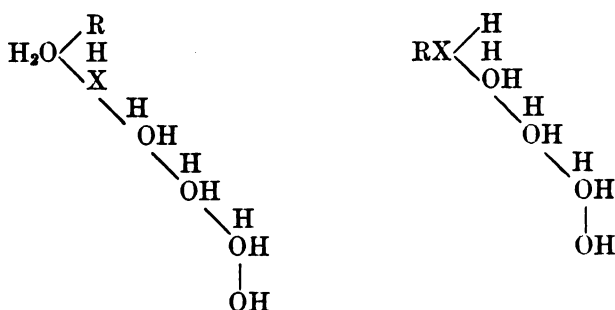
*Hydration.*—At present no very definite conception is attached to the term hydration. From the point of view advocated in this communication, the process may be of two kinds, according as it involves either hydrolation or hydronation. It is assumed that the primary product is a simple hydrol; this may undergo change in two ways and give rise either to a simple or a compound hydrone or to a poly-hydrol. In the former case, compounds such as the following are produced:—



It cannot be supposed that the number of molecules which can be associated in closed hydrone chains is unlimited—probably, as in the case of carbon compounds, a superior limit is soon reached. Hydrone, in this state of combination, is to be regarded as withdrawn from the sphere of action and as exercising a screening effect on the molecule with which it is associated.

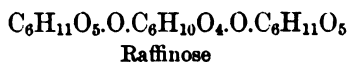
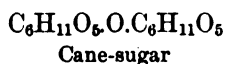
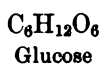
In the case of composite electrolytes, on the other hand, the molecules of the solute may be thought of as hydrated in a way which does not deprive

them of their activity but, on the contrary, enables them to exert their influence at a distance—thus :



The length of such chains would depend on the character of the competition within the solution. Such chains are possibly the conveyors of the current in a liquid electrolyte—they must be thought of as constantly subject to attack from outside by other hydrolated molecules: therefore, as being constantly broken down but remade as constantly.

Reference is made in the following communications (VIII, p. 108; X, p. 130) to the remarkable manner in which the three sugars



reduce the conductivity of salts in solution—practically in proportion to the number of oxygen atoms which they contain. It is therefore probable that each oxygen atom becomes hydrolated (if not polyhydrolated) and that the great influence exerted by the sugars in solution is the consequence of the association of hydrol in this manner with their molecules; as a result, they not only become powerful dehydrolating agents and by their action on hydrolated salt molecules reduce these latter to an inert condition, but are also eminently attractive of the hydrol and hydrone in water and consequently influence the osmotic properties generally of the solution.

It should be pointed out that in presence of hydrolated compounds the equilibrium conditions in the water present in the solution will be disturbed and therefore different from those in ordinary water. Consequently, it is to be expected that the proportions in which the two constituents of a composite electrolyte are present in a simple solution will be altered when another substance is introduced into the solution which modifies the composition of the water—and that no amount of dilution will quite restore the equilibrium. The behaviour of mixtures of electrolytes and of mixtures of electrolytes with non-electrolytes is apparently such as to be expected from this point of view.

*Ionic Properties.*—Whether the distribution of affinity in such chains as are referred to above be equal throughout or at a maximum at their origin is uncertain. The degree of affinity with which hydrol and hydrone are held in the molecule must depend on the nature of the compound  $RX$  and will vary according to the influence exerted by  $R$  upon the negative radicle  $X$ —according as  $X$  is more or less neutralised by  $R$ . Hence also the difference in the conductivity values of different electrolytes. I doubt whether the conception of a constant atomic charge introduced by Helmholtz be defensible from the point of view advocated in this communication. It has recently been admitted by Larmor, in his Wilde lecture, that the structural conceptions of chemists are to be regarded as having something more than a mere symbolic meaning. If we accept the geometric conceptions introduced by Barlow and Pope—which undoubtedly are of the first importance as correlating structure with crystalline form and as affording a means of expressing relationships which have hitherto eluded treatment—we must suppose that volume plays a determining part and it may well be that Faraday's law will find a simple interpretation in volume considerations—that the relation of equality observed among electrolytes is the outcome of an equality in the number of volume units dealt with, just as when water is forced through a series of connected tubes differing in diameter the amount displaced in unit time is regulated entirely by the amount forced through the tube of least diameter.

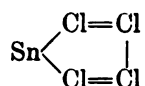
I have already put forward the contention that the conductivity of a binary solution cannot be ascribed to one of the substances only and that the current conception of molecular conductivity is a misconception. The opinion seems to be generally held that conductivity is a direct measure of the extent to which the molecules of the electrolyte share in the process of electrolysis—that the proportion of molecules active in two equivalent solutions may be deduced directly from their molecular conductivities. Such a conclusion is at least open to question—to take an example, that of hydrogen fluoride. It is supposed that few only of the molecules of this hydride are active in solution (dissociated) in comparison with the number active in an equivalent solution of hydrogen chloride, partly because the fluoride is present to a considerable extent in the form of associated molecules and partly because it resists dissociation more than the chloride does. It is far more probable that, owing to the intense affinity of hydrogen for fluorine, but a small proportion of composite molecules ( $H_2O < \overset{H}{F}$ ) in which the hydride is distributed, is formed in the solution; moreover, that the elements of hydrol are held so firmly in the hydrolated

molecules  $\text{HF} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$  that they are far less readily electrolysed than are the corresponding hydrolated hydrogen chloride molecules.

Again, the caustic alkalis have only about half the molecular conductivity of the strong acids. This might be supposed to be due to the presence in solution of a large proportion of associated molecules of the alkali; but a hydroxide such as tetramethylammonium hydroxide has practically no greater conductivity than potash or soda, and yet it is probable that it would exist in solution in an associated form to a far less extent than either of these. It appears probable that the elements of hydrol are held far more firmly by the alkalis than by even the strongest acids.

*Electrolytes and Non-electrolytes.*—Carbon compounds occupy a pre-eminent position as non-electrolytes. This is accounted for without difficulty as a consequence of the fact that when its four units of affinity are satisfied carbon does not manifest any appreciable degree of residual affinity; moreover, its influence over other elements, especially oxygen and chlorine, is altogether remarkable. In other words, carbon compounds are not electrolytes because only those negative elements give rise to electrolytes which assume more than one valency.

To account for the difference met with in the case of a number of metals between the lower and higher chlorides, for example, it is probably necessary to admit more or less profound structural differences and changes in the distribution of affinity consequent on the presence of an excess of chlorine. It is at least doubtful whether any metal have more than one valency—the manifestation of residual affinity is not improbably a non-metallic property. From this point of view, a compound such as stannic chloride—a non-electrolyte—may be represented by the formula:



The difference between it and the lower chloride may be supposed to consist in the fact that the latter and other chlorides which are simple electrolytes in the liquid state resemble water in that they are capable of existing in several different molecular states: to an extent, in fact, which makes the formation of tripartite systems possible without the intervention of other substances.

*Compressibility of Solutions.*—Solutions are often to a very considerable extent less compressible than water; the dissolved substance must therefore, directly or indirectly, exercise an influence within the solution tending to cause its compression. This is the phenomenon discussed by Nernst and others under the designation electrostriction.

Apparently, solutions of acids are less compressible than those of salts; those of ammonium salts come next, following which come those of lithium, potassium and sodium; solutions of nitrates are somewhat more compressible than those of chlorides, those of sulphates considerably less compressible. Unfortunately, the data at disposal are not deduced from observations made under comparable conditions, as only volume-normal solutions have been examined; consequently, no strict deductions can be drawn from them; it is clear, however, that substances fall into much the same order when arranged inversely according to compressibility as they do when arranged according to conductivity and hydrolytic activity.

Hence it may be assumed that the compressibility is dependent mainly, if not entirely, on the number of molecules of the solute which are rendered active by hydrolyation, viz., conversion into effective bipartite composite molecules of the type  $RX < \begin{smallmatrix} H \\ OH \end{smallmatrix}$ , the compressibility being inversely proportional to the number of such molecules.

*Other Properties.*—It is probable that the peculiarities manifest in the case of aqueous solutions generally are often expressions of an aqueous thirst conditioned by the tendency of the hydrol molecules effectively associated with the molecules of the solute by the force of residual affinity to couple with their kind in the manner represented on p. 86. In the case of composite electrolytes this argument is applicable to the two isodynamic complexes in solution.

Thus, if the viscosities of solutions be contrasted, it is obvious on comparing the viscosities of acids with those of their sodium salts that the difference is small in the case of strong, and large in the case of weak acids. Regarding the manifestation of viscosity as in the main a process in which the bipartite composite molecules are torn asunder as similar molecules and the molecules of the solute are forced over their surfaces, solutions containing a small proportion of such molecules—those of weak acids—would obviously be slightly viscous in comparison with those from which, for example, a large number of hydrol molecules can be torn off and converted into ordinary water.

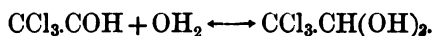
From the point of view here advocated, the depression of the freezing-point and of the vapour-pressure of water by salts—apart from the dissociation effect which these latter produce in the water—is attributable, in like manner, to the attractive influence exercised by the bipartite composite molecules aforesaid and to be proportional to their number.

*Optical Properties.*—The difference in the refraction equivalents of acids and their salts, which is small in the case of strong and large in the case of weak acids, is again attributable to the different influence exercised on

refractive power by the hydrol and hydrone associated with such compounds in solution, the difference being small in the case of strong acids, as the amount in association is more nearly the same in the case of acid and salt, whilst it is large in the case of weak acids, as only a small proportion of composite molecules are present in solutions of these acids, but a considerable proportion in solutions of their salts.

Perkin's observations on the magnetic rotatory powers of the acids and of their aqueous solutions, however, show clearly that discrimination must be exercised in explaining their peculiarities and that there are underlying complexities which need to be taken into account. In the case of the oxygenated acids, the change in rotatory power on adding small proportions of water is considerably less than is accounted for by the water itself, *i.e.*, the water enters into combination in a manner which involves a reduction in the magnetic rotatory power, but the extent to which this is the case diminishes as the dilution is increased. In the case of the halhydrides and other haloids, however, the molecular rotatory power of solutions is greater than the sum of the rotatory power of the anhydrous substance and of the water—the more so the greater the dilution.

In seeking for an explanation of these differences, it is necessary to take into account Perkin's observations on chloral and chloral hydrate, which show that the "water" fixed by the aldehyde has less than half the value of ordinary water. It is generally supposed that an aldehydrol is formed,



A similar explanation may be given of the change produced on adding small proportions of water to sulphuric and nitric acids. It is also not improbable that "hydrolation" should involve a diminution in rotatory power in the case of the halhydrides and haloids and of salts generally; the increase observed may be accounted for, however, if it be assumed that hydronates of the type  $\text{RX}:\text{OH}_2$  are present in solution. Such compounds belong to the ethenoid or unsaturated class; compounds of this type, it is well known, exercise a greater optical effect than do saturated compounds. Hydrols, on the other hand, may be expected to have a relatively small effect.

One other use that may be made of the foregoing considerations remains to be mentioned, *viz.*, their application to the explanation of the effects produced at surfaces: such, for example, as Brownian movements, the evolution of heat on moistening powders, decoloration of solutions—including the withdrawal of dye stuffs by charcoal and other neutral materials—the flocculation of soils and Liebreich's "dead space" phenomena.

A plausible explanation of most if not of all of these effects may be given on the assumption that all surfaces in contact with water become more or less hydrolated and that in virtue of this condition they influence hydrolated molecules in the neighbouring liquid by withdrawing the elements of hydrol from them. From this point of view, the fact noted by Liebreich that, in dilute solutions of sulphurous and iodic acids, change first takes place in the axis of the tube in which the liquid is placed may be the consequence of partial dehydration of molecules in the neighbourhood of the surface of the tube and the consequent diminution in the number of potentially active molecules in passing from the axis of the solution to the periphery. The deposition of "dye stuffs" present in solution as loosely hydrolated "colloid" molecules may be accounted for in a similar manner—in fact, the explanation may be applied generally to the precipitation of colloids from solution by the addition of salts. The "inactive" region which, as Liebreich has shown, exists at the surface of an aqueous solution is probably one in which there is an excess of hydrol molecules—in which, consequently, hydrolated molecules become more depleted of hydrol than in the interior of the liquid, where there is an excess of water. The phenomena of surface tension may also be attributed to the preponderance of monads in the surface layer of a liquid.

The interpretation of the phenomena of chemical change and of electrolysis now put forward has the advantage that it involves the recognition of the essential unity of behaviour of the closely allied elements, oxygen and chlorine, for which I contended so strongly in the discussion at Leeds in 1890.\*

But the conditions in solutions are represented as very complex and it will probably be more than difficult to evaluate the individual factors even in an approximate degree. One of the most essential steps to be taken is the determination of the condition of the water itself in a solution by direct measurement of vapour pressure, a task of no slight difficulty—to this end it is desirable to improve and simplify the method of determining vapour pressure at any desired temperature.

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VII. *The Relative Efficiencies of Acids as deduced from their Conductivities and Hydrolytic Activities.* By H. E. ARMSTRONG and E. WHEELER.

It is commonly stated that nitric and chlorhydric acids are practically equivalent in strength and that sulphuric acid (contrasting molecular proportions) is somewhat stronger than either: the electrical conductivity

\* 'B.A. Report,' 1890, p. 326; 'Zeits. phys. Chem.,' 1891, vol. 7, p. 418.



values on which this conclusion is based appear to have been determined in volume-normal solutions; in no case has the effect due to variation in such solutions in the amount of water displaced by the acid or of that apparently withdrawn by its hydration been taken into account. When the values deduced by R. J. Caldwell, using cane-sugar and gramme-molecular weight-normal solutions of chlorhydric acid,\* are contrasted with those obtained by R. Whymper, using nitric acid, the difference is seen to be very considerable (the velocity constant at 25° being 504 in the one case, 465 in the other), far greater indeed than is observed in the case of the more dilute solutions.

Although—apart from the discrepancies conditioned by variations in the concentration—the conclusions based on other methods of contrasting the strength or affinities of acids appear to be broadly in agreement with those based on the determination of electrolytic conductivity or of hydrolytic activity, there is lack of evidence to what extent the differences are the expression of intrinsic peculiarities.

The method of contrasting the behaviour of substances in dilute solutions which has been so much in vogue of late years is obviously that which is most likely to render their specific properties inconspicuous and it is surprising that it has so long enjoyed popularity; it is even more surprising that, in the case of concentrated solutions, the practice should have so long prevailed of regarding absolute volume as of consequence and of disregarding altogether the great difference in the relative molecular proportion of agent and solvent which such a method of treatment often entails; had we ever given the subject consideration from a chemical standpoint, this remarkable oversight could never have been allowed in practice. For a similar reason the treatment sulphuric acid has received is altogether inconsiderate—that the acid which every chemist must recognise is far the strongest should have been allowed to pass as only of moderate strength (about two-thirds that of nitric acid) is clear proof that the critical faculty has been suppressed by the influence of authority and of fashion.

The experiments referred to in this communication have been made with a view of contrasting the behaviour of the three common acids—nitric, chlorhydric and sulphuric—as hydrolytic agents when associated with water in various proportions, in order to compare the estimates of their relative strengths thus arrived at with those deduced from the electric conductivities of the solutions, as well as in the hope of obtaining further evidence as to the exact nature of the processes of hydrolysis and electrolytic conduction.

*Determination of Hydrolytic Activity.*—The method adopted is that described in previous communications of this series. In determining the

\* 'Roy. Soc. Proc.,' A, vol. 78, p. 287.

activity of 1/10 and 1/20 normal acids, however, the inversion was usually observed during its later stage. The temperature in the polarimeter tube having been adjusted at 25° and a reading taken, the tube was set aside at 25° until about 12 hours afterwards, when the next reading was taken; subsequently, observations were made every hour. The small errors in the readings during the later stages, when the change is slow, affect the value of the constant less than the larger errors which necessarily attend observations made during the earlier stages, when the extent to which change takes place is much greater. The majority of the observations were made in mercury green light.

The results recorded in Table I are those obtained by using a gramme-molecular proportion of each agent together with one-half of a gramme-molecular proportion of cane-sugar and 1000 grammes of water (or  $1000/18=55.5$  molecular proportions).

Table I.

	I.	II.	III.	IV.	Mean.
$\text{HNO}_3 + 55 \cdot 5\text{OH}_2$ .....	466	469	468	469	468
$\text{HCl} + 55 \cdot 5\text{OH}_2$ .....	500	499	499	499	499
$\text{H}_2\text{SO}_4 + 55 \cdot 5\text{OH}_2$ .....	551	554	552	552	552

The rates of change observed in the case of the three acids are very different and it is obvious that equally concentrated solutions, *i.e.* solutions which contain equivalent proportions of the anhydrous substances—are not equally active. Bearing in mind the fact that the three compounds undergo hydration to different extents and also the argument developed in Part I of these Studies and in the Communication on the Nature of Osmotic Effects by one of us, it is clear that solutions containing equivalent proportions cannot be of equivalent strength. To determine the strength at which they produced equal hydrolytic effects, the stronger acids were diluted, until, in each case, the activity was equal to that of the weakest. The results were as follows:—

Table II.

$\text{HNO}_3 + 55 \cdot 5\text{OH}_2$ .....	468		
$\text{HCl} + 55 \cdot 5\text{OH}_2$ .....	499	$+ 6\text{H}_2\text{O}$	436
		$+ 3\text{H}_2\text{O}$	469 : 471
$\text{H}_2\text{SO}_4 + 55 \cdot 5\text{OH}_2$ .....	552	$+ 8\text{H}_2\text{O}$	461
		$+ 7\text{H}_2\text{O}$	469 : 469

The relative values thus arrived at,



are entirely rational; but as we have no means at present of determining the value of  $x$  in the case of nitric acid, the actual extent to which the various acids may be regarded as "hydrated" in solution is uncertain.

To determine the extent to which their activity is reduced by dilution, the rate of inversion was determined in solutions containing 1/10 and 1/20 of a gramme-molecular proportion of acid per 1000 grammes of water. The velocity constants arrived at are recorded in Table III.

Table III.

Acid.	1/10 N.			1/20 N.
	I.	II.	Mean.	Mean.
$\text{HNO}_3$ .....	32.6	32.6	32.6	15.8
$\text{HCl}$ .....	34.2	33.8	34.0	16.7
$\text{H}_2\text{SO}_4$ .....	43.1	42.9	43.0	21.1

It will be seen that, in the dilute solutions, the difference between nitric and chlorhydric acids is slightly less than in concentrated and that the activity of sulphuric acid is far less impaired by dilution than is that of the other acids, the difference between it and the other acids in dilute solutions being considerably greater than in concentrated. The differences between the acids in weak solutions are far beyond those to be expected on the assumption that the acids affect the concentration of the solution in the manner in which they affect that of the stronger solutions—by the withdrawal of water. It is especially noteworthy that the diminution in activity on reduction to decinormal strength is not proportional to the dilution but about 1.5 times as great, although on further dilution to 1/20 the reduction is about proportional to the dilution; it is therefore clear that water has a specific effect in diminishing the activity of the acid, this effect being least in the case of sulphuric acid and greatest in the case of nitric acid.

These differences in behaviour of the three acids are presumably of considerable significance, as throwing light on the process of hydrolysis, especially as showing that it is a process in which water and the hydrolyte are in competition and that the former is either more attractive of or has greater influence over the hydrolyst.

The discrepancy is far greater, however, when acids of equal conducting power are compared as to their hydrolytic activity.

To reduce the molecular conductivity of sulphuric acid to that of chlorhydric acid in a weight-normal solution, the strength of the solution must be raised until 2.15 gramme-molecular proportions are present per 1000 grammes of water; the hydrolytic activity of acid of this strength at 25°, determined in a solution containing half a gramme-molecular proportion of sugar, was found to be  $K=1818$ . An equally concentrated solution of nitric acid gave the value 1452; a similar solution of hydrogen chloride the value 1692.

In view of the difficulty of determining the rate when the change is proceeding rapidly, it may be desirable to place on record the values of the constant deduced at intervals of five minutes.

Table IV.

HCl.	HNO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .
1684	1456	1834
1692	1445	1828
1683	1458	1801
1697	1444	1819
1701	1450	1808
1701	1455	1827
1692	1456	1812
1699	1451	1807
1689	1451	1827
1677	1457	1818

In order that the various values may be compared, they are collected together in the following Table V:—

Table V.—Hydrolytic Activities of Acids at 25°.

	HNO <sub>3</sub> .	HCl.	H <sub>2</sub> SO <sub>4</sub> .	
2.15 N*	675	787	845	
N	468	499	552	
N/10	326	340	430	
N/20	316	334	422	
Expressed as Ratios.				
2.15 N	144	157	153	
N	100	100	100	
N/10	69.6	68.1	77.9	
N/20	67.5	66.9	76.4	
—	100	107	180	Solutions of equal conductivity.
2.15 N	100	99	125	Solutions of equal concentration.
N	100	107	118	" " "
N/10	100	104	132	" " "
N/20	100	105	133	" " "

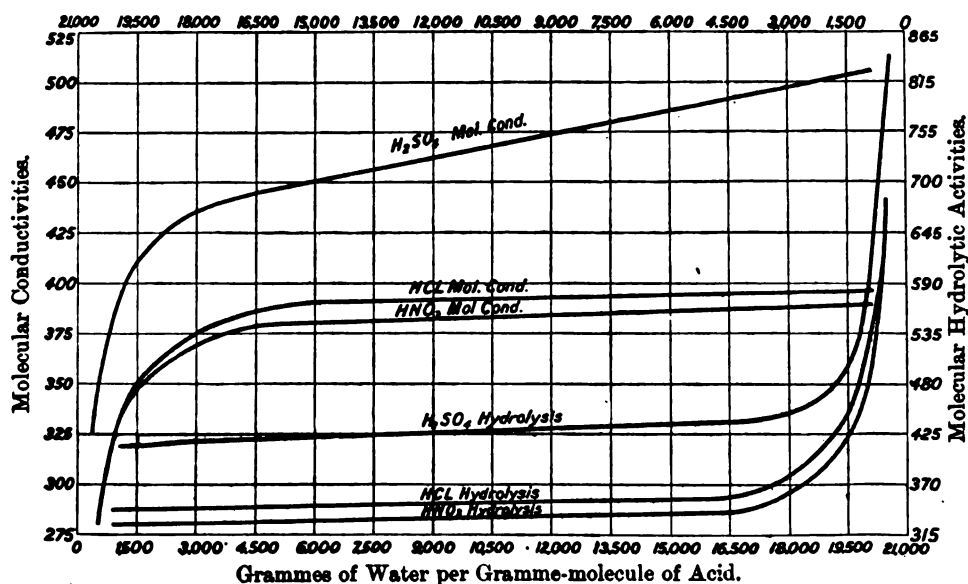
\* The values in this section of the table are the molecular hydrolytic activities obtained by multiplying the observed velocity constants by the weight-normality factors in the first column.

The molecular conductivities at 25° of the various solutions used were found to be as follows :—

Table VI.

	HNO <sub>3</sub> .	HCl.	H <sub>2</sub> SO <sub>4</sub> .	
2·15 N	281·6	278·7	330·4	Solutions of equal hydrolytic power.
N	329·4	330·0	395·6	
N + xH <sub>2</sub> O	329·4	334·6	403·8	
	(x = 0)	(x = 3)	(x = 7)	
N/10	383·1	391·6	468·9	
N/20	391·1	395·5	505·9	
Expressed as Ratios.				
2·15 N	85·5	84·4	83·6	
N	100	100	100	
N + xH <sub>2</sub> O	100	101	102	
	(x = 0)	(x = 3)	(x = 7)	
N/10	116	118	118	
N/20	119	120	127	
2·15 N	100	101	122	Solutions of equal hydrolytic power.
N	100	99	117	Solutions of equal concentration.
N/10	100	100	120	" " "
N/20	100	102	122	" " "
N/20	100	101	129	" " "

It is clear that the two methods afford very different results, dilution having a contrary influence on hydrolytic activity and on apparent molecular conductivity, diminishing the former and increasing the latter; specific differences are also manifest between the acids, nitric acid being most



sensitive to dilution, chlorhydric being affected to a slightly smaller extent and sulphuric very much less. The results are represented in a more obvious manner in the graph on p. 100. A point of some interest is the marked tendency to an alteration in the activity of chlorhydric as compared with nitric acid in concentrated solutions; this may be ascribed, with some probability, to the separation of hydrogen chloride from chlorhydric acid ( $\text{HCl.OH}_2$ ) as the solubility limit of the former is approached and is a justification of the contention that two such substances are to be distinguished: in other words, of Lavoisier's conception of oxygen and of the now almost discarded view that oxygen is a constituent of all acids.\*

In electrolysis only solvent and solute are reciprocally concerned, no substance entering into competition with the solute for the solvent; in hydrolysis the solvent influences both hydrolyte and hydrolyst, hence the difference in the phenomena.

Acids, presumably, have almost unlimited activity when highly concentrated, water playing the part of a mere catalyst, it may be supposed; the acid, on the other hand, is doubtless the effective catalyst in dilute solutions, to an extent which increases as the dilution is increased. The acid being shared by the water and the hydrolyte as the solution is more and more diluted, the competition for the acid between the water and the hydrolyte becomes more and more effective in that the hydrolyte suffers the most; indeed, it is probable that only a very small proportion of the total amount of acid present is effective, otherwise it would be difficult to understand why acids are so weak in comparison with enzymes.

The activity of enzymes is altogether extraordinary, a quantity of invertase, certainly less and perhaps considerably less than 10 milligrammes in weight sufficing to hydrolyse 21.3 grammes of cane-sugar dissolved in 250 c.c. of water within 30 minutes, whereas, in presence of one-fourth of a gramme-molecular proportion of hydrogen chloride (9.1 grammes), the same amount of sugar is hydrolysed only after about 48 minutes; using 0.91 gramme of the chloride, the complete change of the sugar is effected only at the end of about 14 hours, 30 hours being required if only 0.46 gramme of chloride be present. It is to be supposed that the colloid molecules of the enzyme have but slight mobility in solution, so that the sugar molecules must be pictured as attacking rather than as being attacked.

\* [July 22.—Later observations confirm this conclusion and show that the conductivity of "hydrogen chloride" tends to lag more and more behind that of hydric nitrate the more concentrated the solution becomes. The hydrolytic values are not yet determined satisfactorily, as the rate of change is so rapid in concentrated solutions that it is difficult to obtain accurate results; apparently hydrogen chloride maintains its superiority. The scale of the graph is too small to show the differences in concentrated solutions.]

The nature of the processes involved in hydrolysis and electrolytic conduction is more fully discussed in the sixth of these communications.

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VIII. *The Influence of Salts on Hydrolysis and the Determination of Hydration Values.* By H. E. ARMSTRONG and D. CROTHERS.

In the first of these communications a method was described which, it was suggested, permits of the evaluation of the average "concentrating effect" exercised by a salt in solution. The method involves the determination of the rate at which cane-sugar is hydrolysed by an acid alone, then of the rate at which it is hydrolysed in presence of a salt and finally of the amount of water required to reduce the rate of change in the presence of the salt to that at which it takes place when no salt is present; this amount of water is taken as the measure of the "concentrating effect."

Although, in the fourth communication, it was spoken of somewhat confidently as one which afforded a means of determining the *average degree of hydration* of a salt in solution, attention was specially called to possible limitations of the method. And in the fifth communication stress was laid on the fact that the solvent power of water is modified by dissolved salts presumably in a variety of ways—not merely by the withdrawal of a certain proportion in the form of water of hydration; moreover, this point of view had been specially developed by one of us in discussing the origin of osmotic effects.

The results recorded in No. IV, relating to the hydrolysis of methylic acetate by chlorhydric and nitric acids in presence of corresponding salts, as was pointed out at the time, were of a somewhat remarkable character, the "hydration values" found for the salts being in all cases much lower than those obtained when using cane-sugar as hydrolyte. It is not to be denied that these departures were treated somewhat lightly; indeed, the assumption that the metallic salt entered into association with the ethereal salt, thereby hindering to some extent the association of the latter with the "hydrolyst," was referred to as being a simple explanation of the results, yet with the *caveat*: "we are not aware, however, that it has been suspected up to the present time that nitrates (the salts which gave particularly low values) are peculiarly active in thus combining." Our express object in making this statement was to imply that we doubted the sufficiency of the explanation.

The apparent "hydration values" deduced were as follows:—

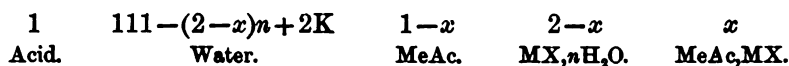
	Chlorhydric acid.			Nitric acid.	
	Sugar.	MeAc.		Sugar.	MeAc.
AmCl .....	10	5	AmNO <sub>3</sub> .....	7	-2
KCl .....	10	8	KNO <sub>3</sub> .....	8	1
NaCl .....	13	10	NaNO <sub>3</sub> .....	11	3

Assuming the degree of "hydration" of the salts to be the same in the presence of either hydrolyte, it should be possible from these results to approximate to the proportion of metallic salt associated with the methylic salt.

The rate of hydrolysis was determined in the system



It was then determined after adding two gramme-molecular proportions of salt, MX, to this system; and, finally, the mixture was examined containing 2K gramme-molecular proportions of water, K being the apparent degree of hydration of the salt MX deduced from the experiments. Assuming the actual degree of hydration ( $n$ ) of the salt to be that found when using cane-sugar, writing  $x$  as the proportion of methylic acetate combined with the salt, the system in the solution would be:—



The rate of hydrolysis in this system being the same as that in the simple solution of acetate, water and acid, if the rate of hydrolysis depend on the ratio of MeAc to water, it follows that

$$\frac{1-x}{111-(2-x)n+2K} = \frac{1}{111} \qquad \text{whence } x = \frac{2n-K}{111+n}.$$

The proportion of hydrolyte combined with the various salts in solution deduced with the aid of this equation is as follows:—

	Per cent.		Per cent.
AmCl .....	8.3	AmNO <sub>3</sub> .....	15.2
NaCl .....	4.7	NaNO <sub>3</sub> .....	13.1
KCl .....	3.3	KNO <sub>3</sub> .....	11.7

These values have a certain significance, although they involve the assumption that the actual hydration values of the salts are those found by means of cane-sugar and no allowance is made either ( $\alpha$ ) for the fact that the proportion of acid to ethereal salt in solution is not quite the same in the



presence as in the absence of the metallic salt or (b) for the water taken up by the ethereal salt and by the MeAc, MX complex or (c) for the possible combination of ethereal salt with the acid.

The order indicated is the same in both series, yet not quite that of the hydration values. It is obvious that ammonium nitrate—for which a minus “hydration” value was deduced—falls into line with the other salts; this salt, in fact, apparently differs less from the other nitrates than does ammonium chloride from the other chlorides. In the case of both chlorides and nitrates the ammonium salts have the greatest effect.

It is known that salts such as calcium chloride combine with methylic acetate and other ethereal salts and therefore are never used in drying them; it cannot well be supposed, however, especially in the case of the nitrates, that combination with the salt takes place *in aqueous solutions* of methylic acetate to such an extent as the calculation above made indicates. And on general grounds the apparent activity of the nitrates in comparison with the chlorides is altogether surprising—especially in view of the positive evidence brought forward in another communication (No. X) in which the combination of salts with cane-sugar in solution is considered—that chlorides are more active than nitrates. But if the values deduced do not afford a measure of the extent to which the salts considered combine with the acetate, they serve to indicate more or less clearly the manner in which the several systems are affected. The greater activity of the ammonium salts as well as of the nitrates in comparison with the chlorides is presumably to be correlated with the fact that the ammonium salts are present in solution to a larger extent than the other salts in the monadic form and that nitrates, in like manner, are probably less polymerised than chlorides.

It should be pointed out that the possible fixation of nitric acid by the salt, although not referred to by Armstrong and Watson, had been taken into account by them and put aside as an unlikely explanation of their results. It is true Ditte\* has shown that both ammonium nitrate and potassium nitrate combine with nitric acid to form acid nitrates; apparently, however, the compounds are for the most part, if not entirely, decomposed by water; and sodium nitrate, which does not form an acid salt, is almost as active as ammonium and more active than potassium nitrate.

In the hope of obtaining further information as to the nature of the changes attending the admixture of the several substances in solution, the alteration in volume was determined which was produced by adding half of a gramme-molecular proportion (37.02) of methylic acetate to a solution containing a gramme-molecular proportion of salt together with 1000 grammes of water

\* ‘Comptes Rendus,’ 1879, vol. 89, pp. 576, 641.

(a weight-normal molecular solution). It was to be supposed that if the salt combined to any considerable extent with the acetate there would be a corresponding alteration in volume and that chlorides would differ markedly from nitrates.

The results recorded in Table I were arrived at by determining the densities of the solutions and dividing the total weight of each solution by the density.

Table I.

$$\text{Methylic acetate } \Delta_4^{\frac{25}{4}} = \frac{0.880735}{0.880765} = 0.88075.$$

	Solution.		Solution + $\frac{1}{4}$ MeAc.		App. vol. of $\frac{1}{4}$ MeAc.	App. mol. vol. MeAc.	Alteration in mol. vol.
	$\Delta_4^{\frac{25}{4}}$	Volume.	$\Delta_4^{\frac{25}{4}}$	Volume.			
Water .....	—	1002.98	0.99777	1039.34	36.36	72.72	—
AmCl .....	1.01266	1040.34	1.01287	1076.70	36.355	72.71	-0.01
			1.01288	1076.69			
AmNO <sub>3</sub> ...	1.02718	1051.53	1.02681	1087.97	36.405	72.81	+0.09
	1.02711	1051.61	1.02679	1087.98			
KCl .....	1.04146	1031.92	1.04090	1068.05	36.13	72.26	-0.46
KNO <sub>3</sub> .....	1.0553	1043.48	1.05402	1079.88	36.395	72.79	+0.07
			1.05403	1079.87			
NaCl .....	1.03611	1021.61	1.03569	1057.77	36.16	72.32	-0.40
NaNO <sub>3</sub> .....	1.05022	1033.22	1.04893	1069.75	36.52	73.04	+0.32
	1.05022	1033.22	1.04896	1069.73			

These results in no way serve to indicate that chlorides and nitrates in solution differ in any special manner in their behaviour towards methylic acetate, at all events to an extent which would serve to elucidate the very different extents to which the two classes of salts affect the rate of hydrolysis. At present, it is difficult to assign any special significance to the figures given in the last column of the table.

With the object of obtaining further information as to the manner in which chlorhydric and nitric acids and their salts influence one another in solution, we have determined the "molecular" electrolytic conductivities in solutions containing 1 gramme-molecular proportion of acid and of salt in 1000 grammes of water and have compared the values with those deduced on the assumption that the two substances retain their specific values; we have in this manner arrived at an estimate of the reduction in the conductivity value due to the admixture of salt and acid. The results are recorded in Table II (p. 106).

These results again serve to show that the difference between chlorides and nitrates is not of the order indicated by the difference in the hydration values deduced by the hydrolytic method, using methylic acetate as hydrolyte. Even if the diminution in conductivity be regarded as falling wholly on the acid

and it be supposed that the hydrolytic activity of the acid is diminished to the extent indicated, the hydration values obtained are in no way accounted for.

Table II.

	Molecular conductivity.		Diminution.	Diminution in molecular solution volume.	
	Observed.	Calculated.			
				c.c.	per cent.
HCl .....	329.23				
NaCl .....	85.91				
AmCl .....	111.78				
KCl .....	112.17				
HCl + NaCl .....	356.12	415.14	14.20	1.13	3.0
HCl + NH <sub>4</sub> Cl .....	399.92	440.96	9.28	1.06	1.9
HCl + KCl .....	402.96	441.40	8.71	0.53	1.1
HNO <sub>3</sub> .....	323.49*				
NaNO <sub>3</sub> .....	76.32				
KNO <sub>3</sub> .....	82.84				
AmNO <sub>3</sub> .....	100.95				
HNO <sub>3</sub> + NaNO <sub>3</sub> .....	345.20	399.81	13.66	1.59	2.6
HNO <sub>3</sub> + KNO <sub>3</sub> .....	374.50	416.33	10.06	1.20	1.7
HNO <sub>3</sub> + AmNO <sub>3</sub> .....	385.60	424.44	9.11	1.02	1.3

\* Owing to an oversight the nitric acid used was slightly below normal strength—a weight-normal solution gave the value 329.4.

To test the influence of the non-electrolyte on each constituent separately of the acid-salt pair, the "molecular" conductivity was determined of acid and salt in weight-normal solutions in presence of a molecular proportion of methylic acetate. The results are recorded in Table III.

Table III.

	Observed molecular conductivity.	Diminution.
		per cent.
HCl + MeAc .....	300.59	8.7
NaCl .....	76.14	11.4
KCl .....	98.87	11.8
AmCl .....	98.70	11.6
HNO <sub>3</sub> .....	292.4	9.5
NaNO <sub>3</sub> .....	69.63	8.8
KNO <sub>3</sub> .....	84.21	9.3
AmNO <sub>3</sub> .....	92.56	8.3

The differences observed between the two classes of salts are again insufficient to afford the desired explanation of their peculiar influence on hydrolytic activity as determined with the aid of methylic acetate.

Assuming that the reduction in conductivity is at least in part due to the reciprocal "dehydrating" influence which the two substances exercise in solution upon one another, the attempt was made to evaluate this dehydrating effect by determining the change in conductivity produced by diluting the solutions. The results obtained are recorded in Table IV. The results do not in any way correspond with those obtained by the hydrolytic method; it is clear that the effect on electrolytic conductivity produced by the admixture of several substances in solution cannot be balanced by the addition of water in the way that the "dehydrating" influence of a salt on the hydrolytic activity of an acid can be annulled by dilution. Whether the substance added be an electrolyte or a non-electrolyte, it will be obvious from the results recorded in Table IV that some effect is produced whatever the dilution but that the effect diminishes as the dilution is increased.

Table IV.

Solution.	+0H <sub>2</sub> O.	+4H <sub>2</sub> O.	+6H <sub>2</sub> O.	+10H <sub>2</sub> O.	+20H <sub>2</sub> O.	+40H <sub>2</sub> O.	+55·5H <sub>2</sub> O.
NaCl .....	85·91	86·65		87·767			
NaCl + MeAc ...	76·14	77·62	78·15	79·19			
NaNO <sub>3</sub> .....	76·32	77·39		78·25			
NaNO <sub>3</sub> + MeAc ...	69·63	70·83		72·56			
NaCl + HCl ...	356·12						417·55
NaNO <sub>3</sub> + HNO <sub>3</sub> ...	345·20						396·29
KCl + HCl .....	402·96			416·20	425·41		
NH <sub>4</sub> Cl + HCl ...	399·92					438·47	

Such results afford proof which cannot well be gainsaid that electrolytic conductivity and hydrolytic activity are processes of a fundamentally different character—affected in opposite directions by changes in concentration or in the medium.

Although the conductivity of the system HCl + MCl in solution is below the sum of the conductivities of its components, its hydrolytic activity is much superior to that of the acid alone—in the case of cane-sugar and sodium chloride to an extent which is expressed by representing the salt as withdrawing 13/55·5 of a molecular proportion of water. But the hydrolyte is itself party to the production of the "dehydrating" effect. To evaluate approximately its influence on the electrolytic conductivity, the conductivity of the system HNO<sub>3</sub>.NaNO<sub>3</sub> was determined in presence of glucose. Using molecular proportions of the three substances and 1000 grammes of water, the apparent molecular conductivity was found to be 261·9 or 345·20—261·9 = 83·3 units less than that of the salt-acid pair alone—a reduction of 24 per cent.

The effect of glucose on the conductivity conditioned by sodium nitrate and by sodium chloride was also determined in solutions containing gramme-molecular proportions per 1000 grammes of water: the reduction produced was found to be 27·4 per cent. in the case of the chloride and 22·8 per cent. in the case of the nitrate. Raffinose,  $C_{18}H_{32}O_{16}$ , was found to have a still greater effect, the conductivity in a solution of sodium chloride being lowered by one-third of a gramme-molecular proportion of this carbohydrate to 68, a reduction of 21 per cent.

The effect of glucose on conductivity is therefore approximately two and a-half times that of methylic acetate and the molecular effect of cane-sugar (as shown in Communication No. X) is  $44\cdot6/27\cdot4$ , whilst that of raffinose is about  $63/27\cdot4$  that of glucose. The significance of such results cannot be overlooked.

It remains to consider what explanation can be given of the remarkable lack of similarity in the behaviour of salts when contrasted by the hydrolytic method, using cane-sugar and methylic acetate.

In view of the evidence now brought forward, it is difficult to arrive at any other conclusion than that the difference is attributable mainly to the peculiarities inherent in the acetate.

The theory put forward in the sixth communication (*ante*, p. 83) involves the assumption that interaction does not take place initially between the nominal hydrolyte and the nominal hydrolyst but between their *hydrolated* molecules; on this assumption, the rate of change will depend largely on the proportion of the one or the other which is present in minor proportion in the hydrolated state. If, then, it be supposed that the affinity of methylic acetate for water is very slight, there would be relatively few effective hydrolated molecules present in a simple aqueous solution; these molecules, moreover, would be very unstable. One effect of adding a salt to the solution would be to concentrate it, as a certain amount of water would enter into combination with the salt and be withdrawn from the solution; the water would also be dissociated by the interposition of the molecules of the salt and the proportion of hydrol in it increased; and this hydrol, together with that attached to the salt, would exercise a more or less powerful dehydrolating influence both on the hydrolyte and the hydrolyst.

The introduction of a salt into the solution should therefore reduce the proportion of effective molecules both of hydrolyte and hydrolyst; these, however, would be affected in different degrees, according to the stability of their composite molecules: the substance which held hydrol but loosely would be more seriously affected than one which held it firmly, so that the effect on

the acid would be relatively slight in comparison with that exercised on the hydrolated molecules of the ethereal salt.\*

If this argument be a sound one, it is clear that the "hydration values" arrived at by the method now under discussion will vary from case to case and that the highest values will be obtained by using hydrolytes and hydrolysts which form relatively stable hydrols in solution. But as several factors are simultaneously operative in every case, *the values deduced will necessarily, in all cases, be apparent values only.* The argument is equally applicable to cryoscopic and other physical methods; as, in reality, all methods of determining such values involve the occurrence of chemical interchanges in solution.

As the influence of a salt or indeed of any third substance, however exercised, necessarily extends both to hydrolyst and to hydrolyte, the "concentrating effect," in some cases, may be such that the increased activity of the hydrolyst more than compensates for the diminished activity of the hydrolyte, whilst in others it less than compensates for the diminution; in the one case the added substance will raise, in the other it will diminish the rate of change. The results brought forward by Senter† may all be regarded from this point of view—they are in no way incompatible, as he suggests, with the conclusion that neutral salt action is due to combination between salt and solvent with consequent concentration of the solution. But "interaction" should be substituted in this sentence for combination, in order that it may be a proper expression of the facts; it has never been contended in these studies of the processes operative in solution that the effects are due to combination alone but, on the contrary, it has always been implied that the changes in the medium are also of supreme importance.

The view here put forward that methylic acetate is a very weak hydrolyte is in accordance with the recognised fact that the carboxylic acids are, with few exceptions, relatively weak acids. It is therefore to be assumed that they are present in solution to but a small extent in the form of hydrolated molecules and that these molecules are easily dehydrolated. As the passage from water to alcohol and ether involves a great diminution in the activity of the compound, it is to be supposed that the introduction of a hydrocarbon radicle in place of the carboxylic hydrogen in acids necessarily conditions a great reduction in the activity of the compound: evidence that this is the case may be found in the simple fact that whilst acetic acid is miscible with water in all proportions, methylic acetate is but moderately soluble.

The superior activity of chlorhydric acid and chlorides in comparison with

\* From this point of view, the comparison of the methylic salts of the various substituted acetic acids with methylic acetate will be of importance.

† 'Chem. Soc. Trans.,' 1907, vol. 91, p. 460; 'Proceedings,' 1908, p. 89.

nitric acid and nitrates may therefore be explained as a consequence of the presence of a larger proportion of the former in solution in the form of hydrolated molecules, the which molecules are also of a higher degree of stability than the corresponding nitrate-hydrols.

Experiments which are being carried out by G. Roche-Lynch show that the hydrolytic activity of bromhydric acid, as tested by means of cane-sugar, is considerably superior to that of chlorhydric acid. Nevertheless, the bromides apparently do not exercise a proportionately greater concentrating effect than corresponding chlorides—although, being salts derived from a stronger acid, they might all be expected to exhibit higher hydration values than the chlorides. The method used, however, is one involving competition between acid and salt and the strong acid may be expected to resist dehydro-lation more than a weaker acid can at the instance of its salts.

To give another instance, it was shown by W. H. Glover and one of us in a recent communication to the Society on the Hydrolysis of Raffinose that the cane-sugar section of the molecule is less readily hydrolysed than is cane-sugar itself. The difference may be explained on the assumption that raffinose is the weaker because it is a less hydrolated hydrolyte: experiments made recently by Dr. Glover seem to show that this is the case, as the "hydration value" of sodium nitrate determined by hydrolysing raffinose by nitric acid in presence of sodium nitrate is  $8\text{H}_2\text{O}$  instead of  $11\text{H}_2\text{O}$ , the value arrived at by R. Whymper by means of cane-sugar.

But that salts are in a sense hydrated in solution there can be no doubt. To evaluate the effect which a salt produces apart from that arising from the mere combination with it of a certain amount of water, it may suffice to compare the action of a salt which apparently is but slightly hydrated with one which seems to be highly hydrated—silver nitrate and sodium nitrate, for example. The apparent hydration values obtained by the sugar method for these two salts are respectively  $5\text{H}_2\text{O}$  and  $11\text{H}_2\text{O}$ . It may be supposed, on account of its low fusing point and its great solubility, that silver nitrate is present in solution to a large extent in the form of simple molecules (monads), probably to a greater extent than is sodium nitrate; the silver salt must, *ex hypothesi*, be hydrated to some extent; but even allowing that approximately only a single molecule of hydrone is attached to it, about four remain as the measure of the influence on the "osmotic" properties of the solution which is produced by the interposition of its molecules among those of the solvent and *the consequent dissociation* of the latter. Assuming it to be present largely in the monadic form, no other salt is likely to produce a much greater "mechanical" effect by the interposition of its molecules between those of the solvent. If, however, four molecules of hydrone be allowed as

the measure of the mechanical interference of a binary salt, it follows apparently that the sodium nitrate molecule is associated with hydrone to the extent of at least  $11-4=7$  molecules. The argument is one to be considered carefully but before it be accepted as final it will be necessary to take into account the possible influence of the degree of intensity of the affinity of a salt for water—whether a salt which has a great affinity for water does not exercise a quasi-mechanical influence, extending beyond the molecules of hydrone which may be regarded as actually linked to its molecules, in proportion to its affinity for hydrol and hydrone, the which influence is necessarily included in any measurement made of its concentrating effect.

In any case, inasmuch as a salt undoubtedly exercises an effect which is the equivalent of a more or less considerable dehydrating or concentrating effect, it is a matter of convenience to express the magnitude of the influence it exercises in a particular system in terms of hydrone molecules, as though these were attached to the salt, although the value thus assigned may differ somewhat widely perhaps from the actual hydration value of the salt, if indeed it have any steady state of hydration—for it may well be that an influence is alone measured.

The argument which is here used in explanation of the effect of salts on hydrolytic activity may also be applied to the results recorded in Tables II, III, IV, showing the effect of admixture on electrolytic conductivity in solutions. Regarding the hydrolated molecules and their isodynamic congeners as the effective carriers of the current, it is to be supposed that owing to the interactions which take place between the composite molecules formed from the admixed solutes and to the change in the state of dissociation of the water conditioned by their joint presence, the proportion of effective molecules is reduced and consequently the conductivity is more or less diminished. From this point of view the effect produced by methylic acetate is to be regarded as almost entirely mechanical, in the sense that it is conditioned by alterations in the state of dissociation of the water consequent on the interposition of the neutral acetate molecules between those of the solvent.

It is noteworthy that the effect of dilution on the acid-salt mixtures is much greater than on those of salt with methylic acetate; probably, in the former case, the acid and salt are present in combination to some extent and water exerts a decomposing influence on the complex.

The larger diminution effected by glucose and the still more striking diminution produced by cane-sugar and raffinose may be in some slight degree ascribable to the formation of compounds with the salts; but such molecules must be thought of as exercising their chief influence in virtue of



the presence in them of long chains of attracting oxygen atoms, so that they act not only mechanically but also by exerting a direct dehydrating effect.

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IX. *The Determination of Optical Rotatory Power.* By R. J. CALDWELL, D.Sc. (Leathersellers' Company's Research Fellow), and R. WHYMPER (Salters' Company's Research Fellow, City and Guilds of London Institute, Central Technical College).

It is known that to determine specific rotatory power to within 1 part in 10,000 it is necessary that the angle measured should exceed  $100^\circ$ , as the method of comparing tints with a triple field polarimeter of the Landolt-Lippich type cannot be relied upon to reveal differences of less than  $0^\circ.01$ . Moreover, as the late Sir William Perkin has specially pointed out, the accurate determination of large optical rotations is rendered difficult by the circumstance that the light from a sodium flame is contaminated with light of longer and shorter wave-lengths: light waves of various refrangibilities being unequally rotated by the sugar at the point of minimum luminosity in yellow light, the observer is confronted with the almost impossible task of matching a blue with a red field. The method of purifying light by liquid filters or gelatin screens recommended by Lippich\* is not only imperfect but also involves so great a reduction of the illumination that difficulty is experienced in taking readings. Purification by spectroscopic means, as carried out by Abney,† is open to the same objection.

Perkin, using a two-field polarimeter, was able to overcome the difficulty by placing a direct-vision spectroscope in front of the eyepiece and made use of this method in his latest determinations of magnetic rotatory power.

In the course of an inquiry into the influence of salts on the rotatory power of cane-sugar, the results of which are discussed in the next communication, we found—especially when using strong solutions—that it was impossible to make satisfactory measurements on account of the colour difficulty referred to above. We were thus led to adapt Perkin's device to a triple-field Landolt-Lippich instrument and to introduce other improvements which have enabled us to overcome practically all the difficulties which ordinarily attend the determination of rotatory power.

The instrument modified was a triple-field Landolt-Lippich polarimeter, graduated to read, with the aid of verniers, to  $0^\circ.01$  and constructed to carry tubes up to 600 mm. in length; the alterations were made by Messrs. A. Hilger and Co. at a moderate cost.

\* 'Zeit. für Instrum.,' 1892, vol. 12, p. 340.

† 'Phys. Soc. Proc.,' 1885, vol. 7, p. 182.

The Jellett-Cornu instrument (purchased from Duboscq many years ago) used in carrying out the work described in previous communications has been modified in a similar manner with equal success.\*

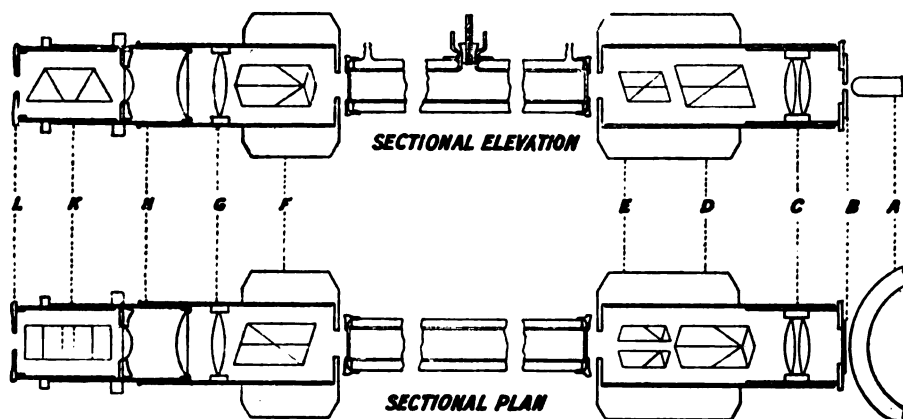


FIG. 1.

In the modified instrument, light from a lamp A passes through a horizontal slit B, which is permanently focussed by means of the achromatic lens C on the half-shadow field E of the polariser D. The slit B can be opened symmetrically and is usually adjusted to a width of 2 mm., so that the setting is made by observation of a band of light across the middle of the ordinary circular field occupying about a quarter of its area. This reduction has in no way rendered the instrument more difficult to use but it should be mentioned that it has been found undesirable to reduce the width of the slit to any greater extent.

A small three-prism combination, mounted in a brass tube, is fitted in front of the eyepiece in such a way that the spectrum can be brought into vertical alignment whatever the position of the analysing nicol. This prism has an angle of dispersion from C to G of about  $16^\circ$ . As the combination is adjusted to give no deviation with the D line, it is necessary to make the aperture L somewhat large, in order that readings may be taken over the whole of the visible spectrum.

If the prism K be sufficiently short, no alteration is necessary in the lenses supplied with the eyepiece.

*Sodium Lamp.*—The ordinary forms of sodium light are insufficiently bright for observations through 600 mm. of strong sugar solution. Doubtless

\* In this instrument, a slit of fixed width previously determined to be suitable is arranged in front of the polarising nicol at E; being practically in the half-shadow field, this slit is permanently in focus, consequently the long tube carrying an achromatic lens at C of the other instrument is therefore unnecessary.

the lamp described by Sir William Perkin would serve in such a case but this is somewhat too expensive for general use, as it involves the use of a large platinum boat and of compressed oxygen. We found that a very bright flame could be obtained by passing finely powdered sodium carbonate into a blowpipe flame along with the air supply. This method, however, necessitated constant use of the bellows during the readings, and gave a light of constantly varying intensity. Ultimately a very cheap and simple instrument was devised, giving a bright and constant light. A Mecker burner (fig. 2) of the larger size was taken off the ordinary base, screwed on to a

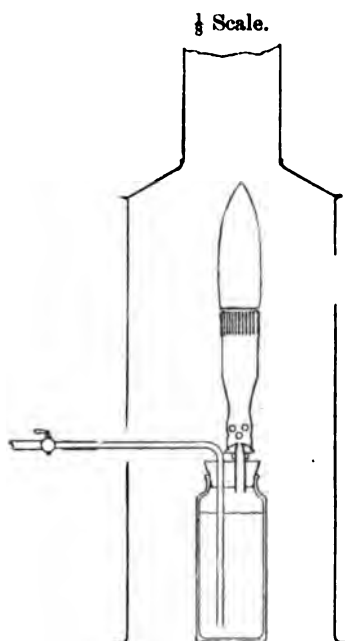


FIG. 2.

piece of brass tubing,  $\frac{1}{4}$  inch internal diameter and  $1\frac{1}{2}$  inches long and fixed in an ordinary glass bottle by means of a rubber stopper. The gas supply is led into the bottle by the glass tube and passes through the powder to the burner; this powder consists of an intimate mixture of equal weights of finely ground, dry sodium carbonate and clean sea sand, the bottle being filled to within 2 inches of the neck. The admixture with sand is necessary in order to prevent the particles of sodium carbonate from caking together and consequently affording a permanent passage for the gas: on account of its high density no sand is carried forward into the burner.

So great is the amount of sodium carbonate blown up, that the whole flame ( $6\text{ inches} \times 1\frac{1}{4}\text{ inches}$ ) is uniformly coloured an intense yellow; it has about 60 candle power in a horizontal plane and can be maintained at this

intensity during at least an hour if the bottle and burner be occasionally shaken.

It is essential that a chimney should be arranged over the burner to carry off the sodium carbonate dust. The form of chimney we have used is shown in the figure; this has the additional advantage that it prevents light from escaping into the room.

In measurements with sodium light the difficulty always arises that the "optical centre of gravity" of the two D lines varies when the intensity of the light varies;\* hence, measurements of the rotatory power of a substance in lights of different intensity will differ among themselves. The Arons-Lummer

\* See Schönrock, 'Zeits. für Instrum.,' 1897, vol. 17.

mercury vapour lamp has been condemned by Landolt for similar reasons. In our experience, the form of the mercury vapour lamp patented by Bastian not only gives a light of constant intensity within the pressure limits of an ordinary 200-volt supply but is eminently suitable for polarimetric measurements with the spectroscopic arrangements we have described.\* We have used the circular form of lamp shown in fig. 1 but a straight tube would undoubtedly be more convenient. When the lamp is burning the mechanism must be tilted slightly to bring the tube into a horizontal plane and it can be brought within  $\frac{1}{4}$  inch of the horizontal slit on the polarimeter. The measurements recorded subsequently were made with a circular lamp which was so placed that light from both sides of the circle entered the slit.

The dispersive power of the prism is not sufficient to separate the two bright yellow lines  $579\mu\mu$  and  $576.9\mu\mu$ . Fairly accordant measurements of rotatory power can be made with this yellow colour, the two lines together appearing to behave as if they had a wave-length  $578\mu\mu$ . When very large rotations are measured, the rotatory dispersive power of the substance is so great that the lines are separated and distinct differences in colour are noticeable between the several parts of the field. For this reason the measurements made with the yellow mercury lines represented in the tables under  $[\alpha]_Y$  are not so trustworthy as those made with sodium light  $[\alpha]_D$  or mercury green light  $[\alpha]_{Hg}$ .

The violet line ( $435.9\mu\mu$ ) affords a light which it is difficult to utilise with our arrangements because the green and yellow which are seen at the same time are comparatively so much brighter and injuriously affect the sensitiveness of the eye. The green light ( $546.1\mu\mu$ ) which is afforded by the mercury spectrum is in every way suitable for polarimetric work, and offers considerable advantages over sodium light on account of its brightness, purity, and constant intensity.

There are six other lines in the neighbourhood, but they are so faint that they could not be seen in our polarimeter at the zero point, even when the slit was closed to the ordinary spectroscopic width. That these lines are negligible is demonstrated by the fact that there is not the slightest indication of any difference in colour in the triple field, with the largest rotation we have measured, viz.,  $150^\circ$ . In all cases the light is of such intensity that observations are easily made through tubes 600 mm. long; series of ten settings of the analyser have seldom shown a greater variety among

\* After long use (perhaps 1000 hours) the lamp is noticeably deteriorated, inasmuch as the yellow light is more intense and the green relatively less intense than in the case of a new lamp.

themselves than 0°02. We regard the measurements we have made with this colour as the most trustworthy of all.

*Method of using Instrument.*—The glass caps for the polarimeter tube should be carefully tested and proved to be optically inactive under the greatest stress to which they can be subjected by the screw caps. Every precaution must be taken to prevent the glasses from being scratched. The solution is poured into the tube by the side opening, which is preferably closed with a small rubber stopper bearing a fine capillary tube, as shown in fig. 1, no air space being left into which the liquid can evaporate.

Although the effect of change in temperature on the rotatory power of cane-sugar is but small, the temperature must be maintained constant in the tube, as variations cause changes in the density and refractive index, thus rendering focussing difficult and the readings uncertain. The thermostat described by Lowry\* has been found to give satisfactory results when an "Albany" rotatory pump is substituted for that he recommended.† Water at 25° is easily circulated through the jacket of a 600-mm. tube at about 1500 c.c. per minute.

Using sodium light, it is necessary to set the polariser at an (half-shadow) angle of about 8°, in order to secure sufficient illumination when using a long tube filled with a solution of sugar. Using the mercury green light and a 200-mm. tube, it is possible to adjust to a smaller half-shadow angle, and thereby increase the accuracy of the observations. The readings are taken in the ordinary way, with the exception that instead of comparing the sections of a complete circle, three squares of equal size are compared across the middle of the ordinary circular field. In observing rotatory power, the refracting prism must be adjusted so that the spectrum is vertical after the analyser has been brought approximately into the correct position for taking the readings.

On referring to Tables I, VI, VIII, IX, and X in the next paper, it will be seen that the "dispersion," viz., the ratio  $[\alpha]_{\text{Hg}} + [\alpha]_{\text{D}}$ , is remarkably constant, being apparently unaffected by changes in the concentration of the sugar, or by foreign substances.

The green mercury light offers so many advantages in practice over sodium light, on account of its intensity and constancy, and because it is less tiring to the eye, requiring, moreover, neither adjustment nor attention, and being

\* 'Faraday Soc. Trans.,' 1907, vol. 3, p. 11.

† This pump, which is made entirely of bronze, possesses the advantage that it runs silently and smoothly as a suction pump, even with a considerable load, and shows no sign of deterioration after six months of continuous use. The pump recommended by Dr. Lowry soon became unworkable, partly by rusting and partly by friction of the moving parts under the strain of sucking water through the jacket of a long tube.

free from fume or dust, that it may confidently be recommended for general use with any half-shadow polarimeter, modified in the manner described. In commercial work with sugar, readings could be multiplied by the factor 0.8486, or a scale might be specially calculated for use with green light.

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- X. *The Changes effected by the Reciprocal Interference of Cane-sugar and other Substances (Salts and Non-electrolytes) in Aqueous Solutions.* By R. J. CALDWELL, D.Sc. (Leathersellers' Company's Research Fellow), and R. WHYMPER (Salters' Company's Research Fellow, Chemical Department, City and Guilds of London Institute, Central Technical College).

The experiments which are described and discussed in this communication were made primarily in the hope of further elucidating the manner in which salts exercise their well-known influence when used together with an acid hydrolyst in effecting hydrolysis; they are an extension of the observations recorded in Parts I and III of this series.

The action of acids alone as well as in presence of their salts on cane-sugar having been determined, it was desirable that the effect produced by salts alone should be studied systematically, as although the subject has already attracted much attention none of the numerous investigations\* hitherto made has been carried out in such a way—with proportions which are equivalent—that the results with different salts are comparable; they cannot, therefore, be made use of for the purpose we have in view.

The considerable acceleration in the rate at which sugar is hydrolysed in presence of salts has been regarded by us in our previous communications as a *concentration effect* produced by the withdrawal from the sphere of action of a certain proportion of water molecules; we therefore, in the first instance, sought to ascertain whether the changes in the rotatory power of cane-sugar in solution conditioned by salts might, in like manner, be regarded as due to changes in the concentration. We feel obliged to conclude that this is not the case, since we find that the effect produced by a salt cannot be cancelled by dilution, except by adding a quantity of water altogether out of proportion to that which it is reasonable to suppose could be withdrawn by any salt; moreover, the reduction effected is in all cases greater than would correspond to the withdrawal of the whole of the water.

Having arrived at this conclusion, we were led to undertake the comparative study of the alterations in a number of the properties—specific

\* Admirable summaries of these are to be found in Lippmann's 'Die Chemie der Zuckerarten,' vol. 2, pp. 1182—91.

rotatory power, density, volume and electrical conductivity—produced by associating cane-sugar with various substances in solution, from the point of view that combination takes place between the two substances; the extent to which this assumption is permissible will be discussed later on in considering the data. We are able to place on record the results of the examination of over 50 separate pairs, all of which have been prepared and measured with the greatest care. The material thus accumulated affords, for the first time we believe, an opportunity of discussing with some approach to certainty the reciprocal effects produced in aqueous solutions by cane-sugar and salts or non-electrolytes; it should be of value also in view of the known importance of salts as factors in vital metabolism and our complete ignorance of their function.

*Preparation of Solutions.*—The sugar used was that sold as *Coffee Sugar* or *Centrifugals*. This, it is well known, consists for the most part of large, well-formed crystals and is remarkable on account of the high degree of purification attained to in its manufacture. At first this sugar was used as purchased but subsequently, throughout the greater part of the inquiry, care was taken to remove all small particles from the large crystals by sifting and to use these latter alone (*cp.* footnote, Table I).

The salts and other substances used were all carefully purified materials, free from acidity.

The solutes were weighed out in a conical flask, due allowance being made for the air displaced. Approximately the right quantity of boiled distilled water was then run in and the solid dissolved by gently warming the flask. After cooling to the temperature of the room, the weight of the solvent was adjusted to the required amount on the balance. It was ascertained that no error was introduced by assuming that the air correction to be applied to the solution might be taken as the sum of the corrections on the constituent parts. As it was found to be necessary to minimise evaporation during filtration of the solutions; the operation was carried out quickly in a tube of the kind described by Lowry,\* using three layers of filter paper strengthened with a piece of silk.

*Determination of Rotatory Power.*—The polarimeter used was the standard Landolt-Lippich triple-field instrument reading to 0°·01, modified in the manner described in the previous communication. The measurements were all made in one water-jacketed tube 600 mm. long, care being taken always to use the same pair of optically inactive glass caps. The half-shadow angle was set to 8° and the slit adjusted to a convenient width at the commencement of the series of measurements, remaining untouched throughout, so

\* 'Chem. Soc. Trans.,' 1904, vol. 85, p. 1558.

that the zero determined before each reading of a solution showed only the slight change due to the variation of the "personal error" from day to day. Occasionally, for the same cause, the zero for one colour would differ slightly from that for another colour. The zero of the instrument was determined to be the same whether the tube were empty or filled with distilled water at 25° the temperature at which all the measurements were made.

*Determination of Density.*—The form of Sprengel tube shown in fig. 1 has been found to be a specially convenient one in use; it has the advantage of being strong and easily wiped and of having no ground-glass joints. The liquid is drawn in through the tube A, the vessel being filled about to D. It is then placed in a thermostat maintained at 25° by means of a Lowry spiral thermo-regulator containing toluene. After about five minutes it is filled to the point B, by bringing some of the liquid contained in a small tube up to the point A and sucking gently at C. When the temperature has attained to constancy, as evidenced by the cessation of movement of the thread of liquid in the capillary tube DC, the liquid is very readily adjusted to the mark B by cautiously applying a piece of filter paper to the point A. The whole

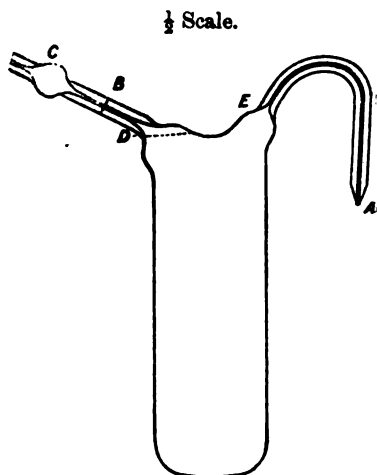


FIG. 1.

of the liquid is at the temperature of the bath except the negligible quantity in the capillary tube A. When the liquid is gently sucked back into the bulb C from the capillary tube AE, the surface tension of the film at E is sufficient to prevent the liquid from running back by gravity to A. The tube is then removed from the bath, cooled in a beaker of water to the temperature of the room and weighed. In our experiments corrections were always made for the air displaced, the humidity of the air being assumed to remain constant at 3.4 mm. pressure of water vapour. Using a tube of 40 c.c. capacity, it is possible to obtain densities accurate to 0.00001. The tube is easily cleaned and is dried by rinsing it out with alcohol, then warming it and sucking a stream of air through it by means of a filter pump.

*Measurement of Conductivity.*—The measurements were made in a resistance vessel of the form shown in fig. 2. The electrodes G are held in position by platinum wires fused in at B. The platinum wires are soldered to stout copper wires CDK at C and the glass tubes HL are fused on to the tubes BL at L. Increased rigidity is afforded and the strain is avoided at the



joints B and C by filling up the tubes BH with molten paraffin wax. A piece of rubber tubing, HDK, fitted over the glass tube BH at H serves to insulate the copper wire from the water of thermostat. Sufficient liquid is introduced at E to fill the U-tube to the level AA and the vessel is closed by connecting its limbs by a piece of rubber tubing EFN. The vessel is immersed several inches below the surface of the water in the bath, hanging from the copper wires CDK which are slipped into the mercury cups MM in electrical connection with the Kohlrausch wheel-bridge.

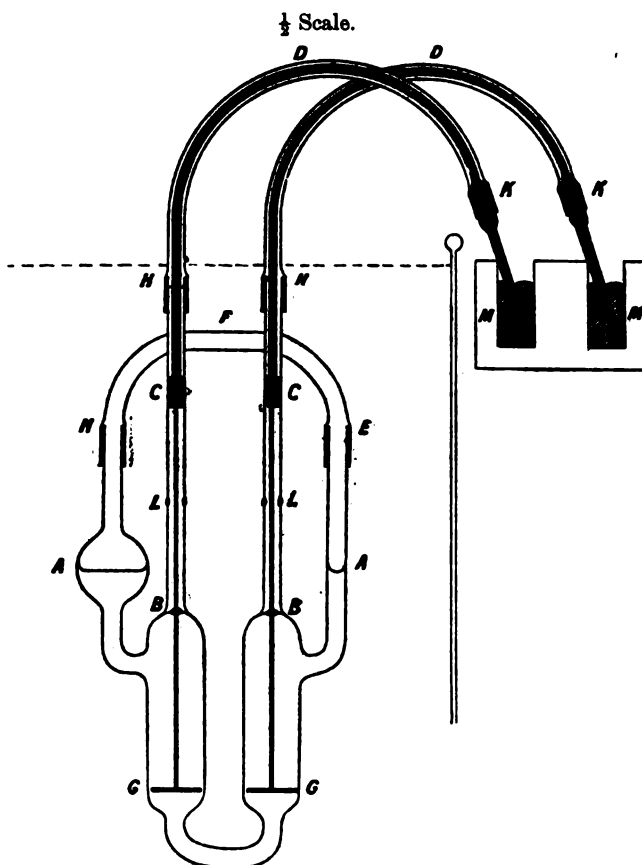


FIG. 2.

This arrangement has the advantage that the connections are made instantaneously without using screws; moreover, the whole apparatus is at the temperature desired, and there is no possibility of the liquid evaporating.

The readings were taken with a Kohlrausch wheel-bridge, inductorium and telephone, using the method described by Bousfield and Lowry.\* The

\* 'Phil. Trans.,' 1904, A, vol. 204, p. 286.

resistance of the electrolytic cell was as nearly as possible balanced by coils of known resistance wound non-self-inductively so that the readings could always be taken at points close to the middle of the wire. Due allowance was made for inequalities in the bridge wire, resistance of the leads and conductivity of the solvent. The water used was prepared by means of the Bousfield still;\* its specific conductivity at 25° did not exceed 0.000002. The results are probably accurate to 1 part in 1000.

*Specific Rotatory Power of Cane-sugar in Solution.*—Although Tollens and several later observers have shown that the specific rotatory power of cane-sugar in solution increases very slightly on dilution, their observations were made under conditions somewhat different from those we have adopted. On this account and in order that we might know the exact behaviour of the sugar we were using, we have examined solutions of weight-molecular strength ( $C_{12}H_{22}O_{11} : 55.5 \text{ OH}_2$ ) and those formed by adding an additional 40, 80 and 120 gramme-molecular proportions of water.

The results are recorded in Table I. The value deduced,  $[\alpha]_D^{25} = 66^\circ.40$ , for weight-molecular strength is in close agreement with that calculated by means of Wiley's temperature coefficient from Tollens' results— $66^\circ.36$ ; and in so far as the observations are concerned our results are in general agreement with those of other observers in showing a slight increase in the value on dilution.

It will be noticed that the dispersion ratio,  $[\alpha]_{H\beta}/[\alpha]_D = 1.178$ , is practically the same in all solutions. This relation also holds good in all solutions we have examined of cane-sugar in admixture with salts or non-electrolytes (Tables I, VI, IX, XI); in discussing our results, therefore, we shall consider only the values obtained in green light. The one noteworthy point is the smallness of the change in the rotatory power of cane-sugar as the concentration is altered. It would seem probable, however, that the degree of association as well as the degree of hydration must vary somewhat as the concentration is varied and that these changes exert an opposing influence on the rotatory power, becoming imperceptible in consequence.

It is noteworthy that liquid ammonia and other anhydrous basic substances are good solvents of sugar and that in all cases the apparent rotatory power in such solutions is high. According to Wilcox,† in fact, sugar affords high osmotic values in solution in pyridine, pointing to association with the solvent. In solutions such as we have examined, the pyridine was in so much water that it is improbable that it produced any effect of its own by

\* 'Chem. Soc. Trans.,' 1905, vol. 87, p. 740.

† Wilcox, 'Journ. Phys. Chem.,' 1901, vol. 5, p. 585; 1902, vol. 6, p. 341.

combining with the sugar. It is, however, by no means improbable that sugar is present in basic solvents to a more or less considerable extent in the form of complex molecules, bearing in mind the very high apparent specific rotatory power which it exhibits in such liquids.

Table I.—Specific Rotatory Power of Cane-sugar in Solutions of various Strengths. One gramme-molecule of cane-sugar dissolved in 1000 grammes of water (55·5 gramme-molecules), diluted with 40, 80 and 120 gramme-molecules of water.

Additional water.	Density of solutions.	$[\alpha]_{\text{Hg}}^{25}$		$[\alpha]_{\text{Y}}^{25}$		$[\alpha]_{\text{D}}^{25}$		Dispersion $[\alpha]_{\text{Hg}}^{25} + [\alpha]_{\text{D}}^{25}$
		Experi- mental values.	Mean.	Experi- mental values.	Mean.	Experi- mental values.	Mean.	
Sugar "A."								
.....	1·10417	78·298	78·30	69·292	69·29	66·438	66·44	1·1785
.....	1·10416	78·293		69·293		66·433		
40H <sub>2</sub> O ...	1·06450	78·311	78·29	69·299	69·28	66·468	66·46	1·1780
	1·06449	78·274		69·262		66·460		
80H <sub>2</sub> O ...	1·04617	78·241	78·25	69·173	69·20	66·479	66·48	1·1770
	1·04619	78·253		69·224		66·491		
120H <sub>2</sub> O ...	1·03571	78·270	78·28	69·211	69·25	66·509	66·51	1·1770
	1·03578	78·297		69·288		66·505		
Sugar "B."								
.....	1·10404	—	78·25			—	66·40	1·1785
40H <sub>2</sub> O ...	1·06448	78·294 78·292	78·29			— 66·421	66·42	1·1787
80H <sub>2</sub> O ...	1·04625	78·300 78·287	78·29			— 66·410	66·41	1·1789
120H <sub>2</sub> O ...	1·03582	78·328 78·294	78·31			— 66·404	66·40	1·1794

The values recorded in this table were obtained at different times—the one set at the beginning, the other at the end of the inquiry. The quality of sugar sold as Centrifugals or Coffee Sugar was used throughout; this consists for the most part of large crystals mixed with a small proportion of fine material, which appears to be only in part the product of abrasion. Sample "A" (referred to in Tables I and IX) was used as purchased, but at an early stage it was noticed that the large and small crystals differed somewhat in rotatory power, thus—

Large crystals.....	$[\alpha]_{\text{D}}^{25} = 66·40$
Small „ .....	66·53
Mixed .....	66·44

Sugar "B" consisted only of large crystals.

In presence of water, ammonia has an effect similar to, although very much weaker than, that produced by caustic potash or soda, reducing the optical activity to a very slight extent; the rotatory power of cane-sugar in liquid ammonia, however, is much higher—especially in dilute solutions—than in aqueous solutions, rising to  $[\alpha]_D = 78^\circ$ .\* Other amines give similar values. As it does not appear probable that compounds containing the similar groups  $O:OH_2$  and  $O:NH_3$  would differ to any considerable extent in their optical effect, these high values are in favour of the assumption that cane-sugar is present in such solutions at least partly in an associated form which is more active optically.

It may be pointed out that our observations show that glycerol has a distinct negative influence. According to Seyffart† glycerol has no effect on the rotatory power of cane-sugar.

#### *Influence of Non-electrolytes.*

The obvious alterations conditioned in solutions of cane-sugar by non-electrolytes (Tables II, VI, VII) are slight, especially in comparison with those effected by salts. Except in the two cases of aldehyde and trichloraldehyde, the apparent specific rotatory power of the sugar in solution is scarcely affected. These compounds and perhaps acetone are, in point of fact, those which it is most likely would prove to be active;‡ it was scarcely to be supposed that the alcohols, methylic acetate or weakly basic substances such as urea and pyridine would tend to combine with sugar in presence of much water. Assuming—as contended in a recent communication to the Society by H. E. Armstrong and W. H. Glover, "On the Hydrolysis of Raffinose"—that the oxygen atom in the ring in the biose carbohydrate is the primary point of attack and the seat of combination, it is not improbable that aldehydes would combine with sugar and give rise to ethenoid

compounds of the type  $\begin{array}{c} \text{C}-\text{C} \\ | \quad | \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O}:\text{OCHR} \end{array}$ ; such compounds, it is to be expected,

would have an enhanced rotatory power, owing to the influence exerted by the ethenoid linkage.§ The difference in the optical change produced by

\* Sherry, 'Journ. Phys. Chem.,' 1907, vol. 11, p. 559.

† Lippmann, p. 1181.

‡ It should be mentioned that reputed compounds of cane-sugar with aldehydes have been described by Schiff. According to Pottévin, the rotatory power is much increased by the addition of a considerable proportion of aldehyde.

§ Cf Armstrong and Robertson, 'Chem. Soc. Trans.,' 1905, p. 1272.

the two aldehydes is in no way surprising; and in view of this difference it is not improbable that acetone is also active in combining but that owing to its symmetrical character the optical effect is slight.

Table II.—Effect of non-Electrolytes on the Specific Rotatory Power of Cane-sugar in Relation to Volume Change in Solution, Gramme-molecular Quantities of each Solute being dissolved in 1000 grammes of Water.

Non-electrolyte.		$[V_{Aq+nE} - V_{Aq}]$ in c.c.	$[V_{Aq+nE+Sg} - V_{Aq+Sg}]$ $- [V_{Aq+nE} - V_{Aq}]$ in c.c.	Alteration in $[\alpha]_{Hg}^x$ in degrees.
	c.c.			
Acetaldehyde .....	(56·74)	43·06	0·00	+0·82
Methylic acetate...	(84·08)	72·43	-0·06	+0·11
Acetone .....	(73·79)	66·41	-0·16	+0·11
Methyl alcohol ...	(40·85)	38·17	-0·44	+0·10
Ethyl alcohol .....	(58·55)	55·21	+0·13	+0·08
Urea .....	(48·04)	44·46	+0·71	0·00
Pyridine .....	(85·55)	78·87	-0·25	-0·08
Glycerol .....	(73·14)	71·83	+0·44	-0·11
Chloral hydrate ...	(97·28)	93·08	-0·08	-0·58

NOTE:  $V_{Aq}$  = vol. of 1000 grammes water at 25° = 1002·98 c.c.

$V_{Aq+nE}$  = vol. of solution of 1 gramme-molecule non-electrolyte in 1000 grammes water.

$V_{Aq+Sg}$  = vol. of solution of 1 gramme-molecule sugar in 1000 grammes of water = 1215·68 c.c.

$V_{Aq+nE+Sg}$  = vol. of solution containing 1 gramme-molecule sugar, 1 gramme-molecule non-electrolyte, and 1000 grammes water.

The figures given in brackets are the actual volumes of non-electrolyte taken per 1000 grammes water.

When the changes in volume which attend the dissolution of the various non-electrolytes in water are considered (Table II, column IV) it is clear that compensating cross influences must be at work which mask the individual effects. The alcohols and pyridine are undoubtedly substances which are far more attractive of water than is methylic acetate; they should all produce somewhat similar effects in modifying the "osmotic properties" of the water and it is to be supposed that those which are the more attractive of water would exercise the greater influence. Yet, as a matter of fact, there is but a slight obvious change in volume on mixing the alcohols with water, whilst the dissolution of methylic acetate—the one neutral compound among the non-electrolytes studied—is attended with a great diminution in volume. It can only be supposed that the real effects are masked in

consequence of structural differences consequent on different modes of packing of the composite molecules which are formed in the solution.

It is important to notice that in the case of some of the non-electrolytes used in our experiments larger proportions than those we have taken are known to produce greater effects. Thus, according to Tollens, the values of  $[\alpha]_D^{20}$  in the case of solutions containing 10 per cent. of sugar are:—

In water .....	66·67
In 1 part water and 3 of alcohol .....	66·83
"                  "          methylic alcohol ...	68·63
"                  "          acetone .....	67·40

As sugar is insoluble in ethylic and but very slightly soluble in methylic alcohol, it is scarcely probable that it combines with either; the greater increase in the apparent specific rotatory power conditioned by a large proportion of methylic alcohol is, therefore, presumably an indication that in such solutions the sugar is present in an associated, more optically active, form. The method adopted by Tollens of deducing the activity of cane-sugar *per se* by extrapolation from observations made with aqueous solutions would not necessarily afford a true value if the sugar complexes are largely, if not entirely, resolved when it is dissolved in water. Tollens, who used solutions containing at most about 70 per cent. of sugar, deduced the value 63·9; a somewhat higher value was deduced by Schmidt, who used solutions containing up to 85 per cent.; it is therefore more than probable that solid sugar has a higher rotatory power than has been supposed.

#### *Influence of Electrolytes.*

The effects produced on adding salts to solutions of cane-sugar are altogether remarkable in comparison with those exercised by non-electrolytes (Tables III, VIII, IX, X). In every case the apparent rotatory power of the sugar is somewhat diminished; the admixture of the salt in solution with the sugar in solution is always attended with a relatively considerable increase in the volume; and the conductivity of the salt in solution is diminished to a surprising extent by the addition of the sugar.

*Change in Rotatory Power.*—Taking into account the effect produced by the three classes of salts, the nitrates obviously exert a smaller influence than the chlorides, whilst the sulphates are more active than the chlorides; caustic alkalis are far superior even to the sulphates.

Inasmuch as compounds of sugars with salts have been isolated, there is every reason to suppose that combination can take place in solution between

Table III.—Effect of Electrolytes on the Secondary Power of Carbon-zinc in relation to the Volume Charge and the Conductivity of the Electrolytes in the Mixed Cell.—Giving molecular quantities of each substance dissolved in 1000 grammes of water

Electrolyte	Volume charge in gms.	$V_{1/2} = \frac{1}{2} \sqrt{\frac{Q}{C}}$	$V_{1/2} = \frac{1}{2} \sqrt{\frac{Q}{C}}$	Secondary power of the cell in volts	Conductivity of the electrolyte in ohm-cm.	Secondary power of the cell in volts
Ammonium nitrate	100.00	1.00	1.00	1.00	1.00	1.00
Potassium nitrate	100.00	1.00	1.00	1.00	1.00	1.00
Sodium nitrate	100.00	1.00	1.00	1.00	1.00	1.00
Lithium nitrate	100.00	1.00	1.00	1.00	1.00	1.00
Silver nitrate	100.00	1.00	1.00	1.00	1.00	1.00
Calcium nitrate	100.00	1.00	1.00	1.00	1.00	1.00
Strontium nitrate	100.00	1.00	1.00	1.00	1.00	1.00
Ammonium chloride	100.00	1.00	1.00	1.00	1.00	1.00
Lithium chloride	100.00	1.00	1.00	1.00	1.00	1.00
Sodium chloride	100.00	1.00	1.00	1.00	1.00	1.00
Potassium chloride	100.00	1.00	1.00	1.00	1.00	1.00
Potassium bromide	100.00	1.00	1.00	1.00	1.00	1.00
Potassium iodide	100.00	1.00	1.00	1.00	1.00	1.00
Strontium chloride	100.00	1.00	1.00	1.00	1.00	1.00
Calcium chloride	100.00	1.00	1.00	1.00	1.00	1.00
Zinc chloride	100.00	1.00	1.00	1.00	1.00	1.00
Sodium sulphate	100.00	1.00	1.00	1.00	1.00	1.00
Zinc sulphate	100.00	1.00	1.00	1.00	1.00	1.00
Magnesium sulphate	100.00	1.00	1.00	1.00	1.00	1.00
Sodium phosphate	100.00	1.00	1.00	1.00	1.00	1.00
Potassium hydroxide	100.00	1.00	1.00	1.00	1.00	1.00
Sodium hydroxide	100.00	1.00	1.00	1.00	1.00	1.00

salts and cane-sugar; it is to be expected, from this point of view, that nitrates would be the least and sulphates the most active. The high values obtained with alkalis are in accordance with the well-known behaviour of cane-sugar toward these compounds.

Although the optical values given in the last column of the table cannot be regarded as an absolute measure of the extent to which combination takes place, there can be little doubt that this is very nearly the case, inasmuch as the nitrates combine to the least and the sulphates to the greatest extent.

Assuming that the salt combines with the sugar in the manner supposed

above, forming compounds of the type  $\begin{array}{c} \text{C}-\text{C} \\ | \quad | \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} : \text{XR}^+ \end{array}$ , the alteration in the optical

effect arises at the  $\text{O} : \text{OXR}$  junction. The effect of this junction will probably not be very different in a series of similar salts, as the modification induced by different metallic radicles is usually not very great; on the other hand, it is to be expected that the effect will vary somewhat more considerably as the negative radicle is varied.

*Change in Electrical Conductivity.*—The remarkable influence of sugar in reducing the electrical conductivity of salts in solution (Tables III, IV, V, XII), to an extent varying between 43 and 51 per cent., might be supposed to be mainly of a "mechanical" nature, *i.e.*, as in part due to direct obstruction of the current and in part to changes in the medium produced by the interposition of the molecules of sugar (*cf.* I, p. 282), particularly as the diminution is produced to much the same extent whatever salt be used.

Regarding the diminution in conductivity as made up of two factors, *viz.* (1) combination of the electrolyte with sugar, (2) mechanical effect of the sugar molecules; assuming, moreover, the latter to be independent of the electrolyte considered, the amount of compound should be deducible in the following manner.

If  $a$  per cent. of the salt be combined and presumably inactive in conducting the current and if  $b$  be the proportional decrease in conductivity effected in other ways by the sugar, the conductivity of the electrolyte in presence of sugar will be  $(100 - a) \times b$  per cent. of its value in the absence of sugar.

The value of the factor  $b$  will vary greatly according to the concentration of the solution; but for the purpose of calculation it is assumed that at any particular concentration it is independent of the electrolyte considered. In weight-normal solutions  $b$  may be taken equal to  $x$  and in solutions diluted with 80 equivalents of water as  $y$ .

The factor  $a$ , *i.e.* the amount of compound, will be proportional in the case



Table IV.—Interference of Sugar and Salt in Presence of varying Quantities of Water.  
One gramme-molecule of sugar and of salt dissolved in 1000 grammes of water  
+ 0, 40, 80 or 120 gramme-molecules of water.

Salt.	Extra water.	$[V_{Aq} + E - V_{Aq}]$ in c.c.	$[V_{Aq} + E + 8g - V_{Aq} + 8g] - [V_{Aq} + E - V_{Aq}]$ in c.c.	Loss in conductivity of salt per cent.	Diminution in $[\alpha]_{Hg}$ of sugar in degrees.
Sodium chloride .....	—	18.58	+ 1.54	44.6	0.95
	20H <sub>2</sub> O	—	—	—	0.69
	40H <sub>2</sub> O	18.35	0.88	29.3	0.51
	80H <sub>2</sub> O	18.08	0.77	21.6	0.33
	120H <sub>2</sub> O	17.95	0.73	17.2	0.23
Magnesium sulphate	—	6.66	+ 3.39	*51.5	*1.26
	40H <sub>2</sub> O	4.47	2.29	33.9	0.80
	80H <sub>2</sub> O	3.11	1.64	*25.4	*0.56
	120H <sub>2</sub> O	2.28	1.71	20.7	0.43
Potassium nitrate.....	—	40.50	+ 1.52	43.7	0.44
	40H <sub>2</sub> O	39.96	1.04	29.2	0.22
	80H <sub>2</sub> O	39.68	0.41	21.7	0.15
	120H <sub>2</sub> O	39.31	0.71	17.1	0.06
Potassium bromide ...	—	36.09	+ 1.40	*45.1	*1.20
	40H <sub>2</sub> O	35.67	0.98	30.0	0.67
	80H <sub>2</sub> O	35.52	0.48	*22.3	*0.46
	120H <sub>2</sub> O	35.42	0.40	17.6	0.30
Potassium hydroxide	—	—	—	—	7.65
	40H <sub>2</sub> O	—	—	—	6.87
	80H <sub>2</sub> O	—	—	—	6.43
	240H <sub>2</sub> O	—	—	—	5.22

Table V.—Interference of Sugar and Salt dissolved in varying Proportions.  
1.0, 0.2 or 0.05 gramme-molecule of sodium chloride dissolved in 1000 grammes of water with and without 1 gramme-molecule of cane-sugar.

Solute per 1000 grammes water.	Apparent molecular volume of salt in c.c.	Volume change per molecule salt in c.c.	Molecular conductivity.	Loss in conductivity per cent.	$[\alpha]_{Hg}^{25}$ in degrees.	Diminution in $[\alpha]_{Hg}^{25}$ in degrees.
1.0 gr.-mol. NaCl...	18.58	1.54	85.91	44.6	—	0.95
1.0 gr.-mol. NaCl + 1 gr.-mol. sugar	20.12		47.610		77.30	
0.2 gr.-mol. NaCl...	17.45	1.35	100.36	44.9	—	0.12
0.2 gr.-mol. NaCl + 1 gr.-mol. sugar	18.80		55.30		78.13	
0.05 gr.-mol. NaCl	17.0	1.4	111.12	45.9	—	0.05
0.05 gr.-mol. NaCl + 1 gr.-mol. sugar	18.4		60.13		78.20	

of varying amounts of any particular salt to the diminution in rotatory power of the sugar by the salt. Since, however, the rotatory power of the compound molecule may not be and probably is not independent of the nature of the salt, the factor  $a$  cannot be taken as quite proportional to the change in rotatory power in the case of different salts; a different factor ( $l, m$ ) must therefore be used for each salt. By making use of the figures marked with an asterisk in Table IV, the four equations obtained are :—

$$\text{MgSO}_4 : (100-a)b = (100-l \times 1^{\circ}26) \times x = 100-51.5 = 48.5 \text{ per cent.}$$

$$(100-a)b = (100-l \times 0^{\circ}56) \times y = 100-25.4 = 74.6 \quad "$$

$$\text{KBr} : (100-a)b = (100-m \times 1^{\circ}20) \times x = 100-45.1 = 54.9 \quad "$$

$$(100-a)b = (100-m \times 0^{\circ}46) \times y = 100-22.3 = 77.7 \quad "$$

Solving these, we have

$$x = 0.370, \quad y = 0.662, \quad l = -24.5, \quad m = -40.4.$$

The values of  $l$  and  $m$  being negative are of an impossible character—a minus quantity of compound being inconceivable.

It is scarcely to be questioned that the first assumption is correct, namely, that the amount of compound of sugar with any particular salt is proportional to the effect produced by that salt on the rotatory power. The error must arise in assuming that the sugar produces a "mechanical effect" which is independent of the salt affected. In the case of barium chloride, to take an example, a large decrease in conductivity is associated with but a small change in the rotatory power and obviously such a result may be taken as confirmatory of this argument.

Although it is impossible apparently to deduce the extent to which combination takes place from a consideration of the conductivity values in the case of salts, a minimum estimate may perhaps be arrived at in the case of the caustic alkalis by another line of argument.

The very marked decrease in rotatory power produced by alkalis, whether ascribable or not to the formation of actual salts in which hydroxylic hydrogen is displaced by metal, must be regarded as evidence that "combination" takes place to a considerable extent, especially in view of the even more remarkable diminution of the conductivity in a solution of an alkali effected by cane-sugar. Assuming, in order to arrive at a minimum value, that the reduction in conductivity effected in the case of sodium chloride (44.6 per cent.) is wholly a mechanical effect and that the alkali is influenced mechanically to an equal extent, if  $x$  per cent. of the alkali enter into combination with the sugar, in the case of sodium hydroxide,

$$(100-x) \times (100-44.6)/100 = (100-79.5).$$

Since  $x = 63$  per cent. it may be assumed that approximately this proportion of compound is formed.

On this assumption, the rotatory power would be decreased to  $[\alpha]_D = 56^\circ$  if the sugar were completely combined with the alkali. It is noteworthy that the value  $56^\circ.8$  has been deduced by Thomson by extrapolation from measurements made with proportions of sugar and alkali such as we used at various concentrations as that of the rotatory power of sodium saccharate in the absence of water.

Regarding the changes in rotatory power as directly proportional to the amount of salt entering into combination with the sugar, if the observed values are contrasted with those thus deduced for alkalis, it would follow that combination takes place to an extent approximating to 7 per cent. in a case such as that of potassium chloride and to 18 per cent. in the case of the iodide. If, however, the rotatory power of the compound formed by potassium iodide be greater than that of the corresponding compound with potassium chloride, this latter estimate will be subject to more or less considerable reduction. The uniformly low values given by nitrates are in accordance with this line of argument, as nitrates are generally regarded as less prone to enter into combination than chlorides.

Far more striking than the effect produced on the sugar by the salt, as indicated by the change in rotatory power, is the surprising diminution by almost one-half in the conductivity of salts in solution which is determined by the sugar—especially when it is considered that this diminution is brought about by the addition of a single molecular proportion of a substance like sugar, ordinarily regarded as a somewhat inert compound, to a mixture of a single molecular proportion of salt with 55.5 molecular proportions of water.

The effect cannot be in any way accounted for by supposing that the salt and sugar enter into combination to the extent required by such an assumption—probably, at the very most, about one-fifth of the change can be ascribed to such an action. It has already been shown, in the first of these communications, that glucose and galactose reduce the conductivity of solution of hydrogen chloride to the extent of about 30 per cent. As it is to be supposed, on general grounds, that the glucoses would combine even more readily than cane-sugar with acids and salts, bearing in mind the manner in which the glucoses are related to cane-sugar, there can be little doubt that the remarkable influence sugars exercise on conductivity is to be correlated with the presence in them of a series of oxygen atoms, the effect being practically proportional to the number of hydroxyl groups (8 and 5) present in the two carbohydrates.

The differences noticeable among the various salts are doubtless ascribable to the differences in the extents to which the salts exist in solution in the monadic form, as well as to differences in the extent to which they enter into combination with the sugar, also to specific differences among the salts affecting conductivity.

The substances most affected, such as barium chloride and zinc and magnesium sulphates, are compounds which are near the saturation point in solutions such as were examined and it is probable that these salts readily undergo polymerisation in such solutions. Apart from these three salts, the order in which conductivity is affected is practically identical with the order of change in rotatory power.

*Volume Changes.*—As shown in the column B—A in Table XII, the admixture of sugars with salts in solution involves, in all cases, a more or less considerable expansion. This result is especially striking in view of the fact already commented on that non-electrolytes, as a rule, do not produce such an effect. There is reason to suppose that the increase in volume is due, at least mainly, to the liberation of water; also that this is conditioned less by the interaction involved in the combination of sugar with salt than by the change in the medium brought about by the increase in the amount of solute which is a necessary consequence of the admixture of the two substances. The change in volume is deduced by a method of comparison which is faulty in that the double effect on the medium, due to the presence of the two solutes in solution, cannot be taken into account. Thus the values in column A are the apparent volumes of the salts in solution in water, those in B the apparent volumes of the salts in solution in presence of sugar: in a solution, therefore, which differs from water in having sugar present in it; the values given in the column B—A are in defect, therefore, to the extent of this difference.

It is noticeable that specially high values are given by salts such as barium chloride and the sulphates. It may be supposed that barium chloride is present in an ordinary aqueous solution, at least to a considerable extent, in a hydrated form; and that on the addition of sugar much of the salt present in this form becomes polymerised, losing water in the process. A similar explanation applies to the sulphates.

On reference to Table IV, it will be seen that the effect produced by the admixture of salts with sugar, however tested, diminishes as the concentration is diminished, showing that the compound produced in concentrated solutions undergoes decomposition on dilution. Caustic alkalis not only give rise to a larger proportion of "compound" but the product is far less affected by dilution than are those formed from salts.

In whatever way the results are regarded, the facts generally appear to be in accord with the hypothesis that a relatively small proportion of a dissociable compound of sugar and salt is produced—in fact, no other explanation seems to be possible of the values given in the last column of Tables III, IV and V, relating to the influence of concentration, whether of salt or of solvent. Characteristic differences are apparent between the various salts, especially when the sulphates are contrasted with the salts containing monad radicles ; but it is obvious that the relationship of the various substances in solution is of a complex character. The extraordinary influence exercised by sugar on the electrical conductivity of salts in solution is a clear indication, however, that no satisfactory explanation of the phenomena can be given without taking into account the manner in which the solvent is modified by the solute—the need, in fact, of regarding the changes as the outcome of reciprocal interferences.

Table VI.—Effect of non-Electrolytes on the Specific Rotatory Power of Sugar "B." One gramme-molecule of cane-sugar in 1000 grammes water with addition of 1 gramme-molecule of non-electrolyte.

Non-electrolyte.	Density of solutions.	$[\alpha]_{\text{Hg}}^{\text{25}}$		$[\alpha]_{\text{Y}}^{\text{25}}$		$[\alpha]_{\text{D}}^{\text{25}}$		Dispersion, $[\alpha]_{\text{Hg}} + [\alpha]_{\text{D}}$
		Experiments.	Mean.	Experiments.	Mean.	Experiments.	Mean.	
Acetaldehyde, $\text{CH}_3\text{CHO}$ .....	1·10181 1·10176	79·061 79·082	79·07	69·923 69·951	69·94	67·074 67·087	67·09	1·1786
Acetone, $(\text{CH}_3)_2\text{CO}$ .....	1·09301 1·09265	78·350 78·370	78·36	69·327 69·337	69·33	66·494 66·522	66·51	1·1782
Methyl acetate, $\text{CH}_3\text{COOCH}_3$ .....	1·09948 1·09929	78·351 78·360	78·36	69·316 69·323	69·32	66·487 66·493	66·49	1·1785
Methyl alcohol, $\text{CH}_3\text{OH}$ .....	1·09635 1·09650	78·357 78·347	78·35	69·327 69·312	69·32	66·476 66·479	66·48	1·1786
Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$ .....	1·09311 1·09309	78·330 78·332	78·33	69·258 69·291	69·27	66·460 66·443	66·45	1·1788
Urea, $\text{CO}(\text{NH}_2)_2$ .....	1·11223 1·11225	78·254 78·246	78·25	69·218 69·211	69·21	66·381 66·386	66·38	1·1788
Pyridine, $\text{C}_5\text{H}_5\text{N}$ .....	1·09806 1·09816	78·228 78·216	78·22	69·168 69·194	69·18	66·338 66·357	66·35	1·1789
Glycerol, $\text{C}_3\text{H}_8(\text{OH})_3$ .....	1·11391 1·11380	78·139 78·146	78·14	69·139 69·153	69·15	66·305 66·311	66·31	1·1784
Chloral hydrate, $\text{CCl}_3\text{CH}(\text{OH})_2$ .....	1·15193 1·15197	77·682 77·690	77·67	68·739 68·717	68·73	65·934 65·906	65·92	1·1782

Table VII.—Volume Changes in Solutions of non-Electrolytes with and without Cane-sugar. One gramme-molecule of non-electrolyte in 1000 grammes water with or without 1 gramme-molecule of cane-sugar.

Solutes.	Density of solutions.	Total volume of solutions in c.c.	$[V_{Aq+nE} - V_{Aq}]$ in c.c.	$[V_{Aq+nE+Sg} - V_{Aq+Sg}]$ in c.c.
Acetaldehyde .....	0·99808	1046·04	43·06	
Acetaldehyde + sugar .....	1·10125	1258·74		43·06
Methylic acetate .....	0·99873	1075·41	72·43	
Methylic acetate + sugar .....	1·09950	1288·05		72·37
Acetone .....	0·98939	1069·39	66·41	
Acetone + sugar .....	1·09227	1281·93		66·25
Methyl alcohol .....	0·99124	1041·15	38·17	
Methyl alcohol + sugar .....	1·09636	1253·41		37·73
Ethyl alcohol .....	0·98982	1058·19	55·21	
Ethyl alcohol + sugar .....	1·09328	1271·02		55·34
Urea .....	1·01210	1047·44	44·46	
Urea + sugar .....	1·11216	1260·85		45·17
Pyridine .....	0·99744	1081·85	78·87	
Pyridine + sugar .....	1·09808	1294·30		78·62
Glycerol .....	1·01652	1074·31	71·33	
Glycerol + sugar .....	1·11396	1287·45		71·77
Chloral hydrate .....	1·06326	1096·06	93·08	
Chloral hydrate + sugar .....	1·15195	1308·68		93·00

Table VIII.—Effect of Electrolytes on the Specific Rotatory Power of Sugar "A." One gramme-molecule of cane-sugar in 1000 grammes of water with addition of 1 gramme-molecule of electrolyte.

Electrolyte.	Density of solutions.	$[\alpha]_{\text{Hg}}^{25}$		$[\alpha]_{\text{Y}}^{25}$		$[\alpha]_{\text{D}}^{25}$		Dispersion, $[\alpha]_{\text{Hg}} \div [\alpha]_{\text{D}}$ .
		Experiments.	Mean.	Experiments.	Mean.	Experiments.	Mean.	
.....	1·10417	78·296	78·30	69·292	69·29	66·438	66·44	1·1785
.....	1·10416	78·293		69·293		66·433		
Sodium chloride, NaCl.....	1·13343	77·350	77·35	68·489	68·49	65·654	65·65	1·1782
Potassium chloride, KCl .....	1·13700	77·441	77·44	68·531	68·54	65·752	65·75	1·1778
.....	1·13703	77·445		68·541		65·743		
Lithium chloride, LiCl.....	1·12088	77·645	77·64	68·710	68·70	65·888	65·89	1·1783
.....	1·12087	77·640		68·693		65·899		
Ammonium chloride, $\text{NH}_4\text{Cl}$ .....	1·11299	77·715	77·71	68·761	68·77	65·981	65·97	1·1780
.....	1·11301	77·713		68·790		65·968		
Barium chloride, $\text{BaCl}_2$ .....	1·24075	77·724	77·72	68·757	68·76	65·939	65·94	1·1786
.....	1·24077	77·723		68·763		65·932		



Table IX.—Effect of Electrolytes on the Specific Rotatory Power of Sugar “B.” One gramme-molecule of cane-sugar in 1000 grammes of water with addition of one gramme-molecule of electrolyte.

Electrolyte.	Density of solutions.	$[\alpha]_{H_g}^{25}$		$[\alpha]_Y^{25}$		$[\alpha]_D^{25}$		Dispersion, $[\alpha]_{H_g} + [\alpha]_D$ .
		Experiments.	Mean.	Experiments.	Mean.	Experiments.	Mean.	
.....	1·10403	78·255		69·242		66·388		
.....	1·10404	78·242		69·235		66·399		
.....	1·10403	78·255	78·25	69·242	69·24	66·406	66·40	1·1785
.....	1·10404	78·242		69·235		66·405		
.....	1·10408	78·239		69·233		66·400		
Silver nitrate, AgNO <sub>3</sub> .....	1·21134	78·080		69·057		66·199		
.....	1·21140	78·077	78·08	69·053	69·06	66·220	66·21	1·1794
Ammonium nitrate, NH <sub>4</sub> NO <sub>3</sub> .....	1·12393	78·067		69·080		66·263		
.....	1·12382	78·056	78·06	69·067	69·07	66·245	66·25	1·1783
Lithium nitrate, LiNO <sub>3</sub> .....	1·12444	78·042		69·056		66·201		
.....	1·12440	78·045	78·04	69·048	69·05	66·221	66·21	1·1787
Calcium nitrate, Ca(NO <sub>3</sub> ) <sub>2</sub> .....	1·16646	78·026		69·044		66·226		
.....	1·16651	78·036	78·03	69·048	69·05	66·224	66·23	1·1782
Strontium nitrate, Sr(NO <sub>3</sub> ) <sub>2</sub> .....	1·22541	77·855		68·887		66·064		
.....	1·22537	77·864	77·86	68·895	68·89	66·054	66·06	1·1786
Potassium nitrate, KNO <sub>3</sub> .....	1·14747	77·813		68·837		66·049		
.....	1·14761	77·804	77·81	68·829	68·83	66·048	66·05	1·1783
Sodium nitrate, NaNO <sub>3</sub> .....	1·14388	77·716		68·745		65·973		
.....	1·14391	77·720	77·72	68·749	68·75	65·978	65·98	1·1779
Barium chloride, BaCl <sub>2</sub> .....	1·24076	77·692		68·749		65·963		
.....	1·24075	77·699	77·70	68·756	68·75	65·957	65·96	1·1780
Ammonium chloride, NH <sub>4</sub> Cl .....	1·11295	77·669		68·704		65·947		
.....	1·11293	77·676	77·67	68·703	68·70	65·942	65·94	1·1779
Lithium chloride, LiCl .....	1·12066	77·623		68·657		65·817		
.....	1·12063	77·613	77·62	68·665	68·66	65·837	65·83	1·1791
Potassium chloride, KCl .....	1·13691	77·423		68·494		65·684		
.....	1·13699	77·418	77·42	68·489	68·49	65·691	65·69	1·1786

Sodium chloride, NaCl .....	1·13340 1·13339	77·298 77·305	77·30	68·382 68·389	68·39	65·596 65·594	65·59	1·1785
Strontium chloride, SrCl <sub>2</sub> .....	1·18004 1·18004	77·134 77·127	77·13	68·245 68·245	68·25	65·426 65·420	65·42	1·1790
Potassium bromide, KBr .....	1·16609 1·16610	77·039 77·057	77·05	68·164 68·169	68·17	65·387 65·368	65·38	1·1785
Calcium chloride, CaCl <sub>2</sub> .....	1·16415 1·16418	76·952 76·963	76·96	68·069 68·079	68·07	65·278 65·289	65·28	1·1789
Potassium iodide, KI .....	1·19349	76·067	76·07					
Zinc sulphate, ZnSO <sub>4</sub> .....	1·22865 1·22866	77·161 77·184	77·17	68·267 68·290	68·28	65·483 65·495	65·49	1·1783
Magnesium sulphate, MgSO <sub>4</sub> .....	1·19321 1·19321	76·991 76·992	76·99	68·095 68·076	68·09	65·307 65·295	65·30	1·1790
Sodium sulphate, Na <sub>2</sub> SO <sub>4</sub> .....	1·19371 1·19369	76·074 76·088	76·08	67·342 67·341	67·34	64·536 64·567	64·55	1·1786
Sodium phosphate, Na <sub>2</sub> HPO <sub>4</sub> .....	1·20309	74·590	74·59					
Potassium bicarbonate, KHCO <sub>3</sub> ..	1·14918 1·15007	77·183 77·166	77·17	68·282 68·284	68·28	65·476 65·474	65·48	1·1785
Potassium carbonate, K <sub>2</sub> CO <sub>3</sub> .....	1·18600 1·18615	73·086 73·077	73·08	64·610 64·609	64·64	62·082 62·087	62·08	1·1781
Sodium carbonate, Na <sub>2</sub> CO <sub>3</sub> .....	1·18079 1·18081	73·007 73·018	73·01	64·625 64·612	64·62	61·991 61·995	61·99	1·1778
Ammonium hydroxide, NH <sub>4</sub> OH ...	1·09486 1·09485	78·006 78·019	78·01	69·005 69·005	69·01	66·198 66·181	66·19	1·1786
Sodium hydroxide, NaOH .....	1·18548 1·18548	70·651 70·651	70·65	62·524 62·536	62·53	59·915 59·945	59·93	1·1789
Potassium hydroxide, KOH .....	1·14023 1·14023	70·608 70·590	70·60	62·478 62·472	62·46	59·933 59·927	59·93	1·1780

Table X.—Molecular Conductivity and total Volume of Solutions of Electrolytes with and without Cane-sugar. One gramme-molecule of electrolyte in 1000 grammes of water with or without one gramme-molecule of cane-sugar.

Solutes.	Density of solutions.	Total volume of solutions in c.c.	$[V_{Aq} + E - V_{Aq}]$ in c.c.	$[V_{Aq} + E + Sg - V_{Aq} + Sg]$ in c.c.	Molecular conductivity of electrolyte.
$NH_4NO_3$ .....	1·02682	1051·90	48·92		100·95
$NH_4NO_3$ + sugar ...	1·12366	1265·75		50·07	57·608
$KNO_3$ .....	1·05531	1043·48	40·50		92·84
$KNO_3$ + sugar .....	1·14761	1257·70		42·02	52·231
$NaNO_3$ .....	1·05035	1033·07	30·09		76·32
$NaNO_3$ + sugar .....	1·14409	1247·50		31·82	42·915
$LiNO_3$ .....	1·02627	1041·09	38·71		56·580
$LiNO_3$ + sugar .....	1·12416	1255·35		39·67	31·615
$AgNO_3$ .....	1·13156	1033·95	30·97		78·50
$AgNO_3$ + sugar .....	1·21129	1248·36		32·66	43·859
$Sr(NO_3)_2$ .....	1·15155	1052·22	49·24		91·52
$Sr(NO_3)_2$ + sugar ...	1·22550	1267·92		52·24	49·990
$Ca(NO_3)_2$ .....	1·08142	1076·44	73·46		88·10
$Ca(NO_3)_2$ + sugar ...	1·16637	1291·39		75·71	48·918
$NH_4Cl$ .....	1·01261	1040·40	37·42		111·73
$NH_4Cl$ + sugar .....	1·11290	1254·09		38·41	63·52
$LiCl$ .....	1·02045	1021·57	18·59		73·43
$LiCl$ + sugar .....	1·12072	1235·47		19·79	40·836
$KCl$ .....	1·04136	1031·92	28·94		112·17
$KCl$ + sugar .....	1·13704	1246·02		30·34	62·11
$NaCl$ .....	1·03616	1021·56	18·58		85·91
$NaCl$ + sugar .....	1·13340	1235·80		20·12	47·610
$KBr$ .....	1·07703	1039·07	36·09		115·55
$KBr$ + sugar .....	1·16607	1253·17		37·49	63·45
$SrCl_2$ .....	1·09646	1056·58	53·60		119·85
$SrCl_2$ + sugar .....	1·17990	1271·85		56·17	65·29
$CaCl_2$ .....	1·07262	1035·78	32·80		123·67
$CaCl_2$ + sugar .....	1·16206	1250·50		34·82	66·07
$BaCl_2$ .....	1·16890	1033·71	30·73		138·94
$BaCl_2$ + sugar .....	1·24061	1249·76		34·08	73·41
$KI$ .....	1·11059	1050·00	47·02		118·34
$KI$ + sugar .....	1·19349	1263·76		48·08	63·697
$Na_2SO_4$ .....	1·11254	1026·62	23·64		94·86
$Na_2SO_4$ + sugar .....	1·19352	1243·65		27·97	49·899
$ZnSO_4$ .....	1·15281	1007·50	4·52		46·776
$ZnSO_4$ + sugar .....	1·22862	1223·83		8·15	22·889
$MgSO_4$ .....	1·10972	1009·64	6·66		50·218
$MgSO_4$ + sugar .....	1·19323	1225·73		10·05	24·361
$Na_2HPO_4$ .....	1·12491	1015·29	12·31		64·06
$Na_2HPO_4$ + sugar ...	1·20309	1233·71		18·03	31·706
$KOH$ .....	1·04041	1014·68	11·70		185·57
$KOH$ + sugar .....	1·13564	1231·30		15·62	45·329
$NaOH$ .....	1·03873	1001·28	-1·70		151·23
$NaOH$ + sugar .....	1·13541	1217·87		+1·69	31·046

Table XI.—Alteration in the Rotatory Power of Sugar conditioned by Electrolytes in presence of varying Quantities of Water. One gramme-molecule of cane-sugar and 1 gramme-molecule of electrolyte dissolved in 1000 grammes of water and diluted with 20, 40, 80, 120 or 240 gramme-molecules of water.

Electrolyte.	Additional water.	Density of solutions.	[ $\alpha$ ] <sub>Hg</sub> .		[ $\alpha$ ] <sub>Y</sub> .		[ $\alpha$ ] <sub>D</sub> .		Dispersion, [ $\alpha$ ] <sub>Hg</sub> + [ $\alpha$ ] <sub>D</sub> .
			Experi- mental values.	Mean.	Experi- mental values.	Mean.	Experi- mental values.	Mean.	
Sodium chloride .....	—	1·13343	77·350	77·35	68·489	68·49	65·654	65·65	1·1782
	20H <sub>2</sub> O	1·10285	77·609	77·61	68·705	68·71	65·928	65·93	1·1772
	40H <sub>2</sub> O	1·08414	77·778	77·78	68·880	68·83	66·010	66·01	1·1768
	80H <sub>2</sub> O	1·06071	77·918	77·92	68·956	68·96	66·203	66·20	1·1778
Potassium hydroxide .....	120H <sub>2</sub> O	1·04685	78·051	78·05	69·088	69·09	66·271	66·27	1·1778
	—	1·14023	70·608	70·60	62·478	62·48	59·933	59·93	1·1780
	—	1·14023	70·590	70·59	62·472	62·48	59·927	59·93	1·1780
	40H <sub>2</sub> O	1·08321	71·382	71·38	63·153	63·15	60·561	60·56	1·1787
Magnesium sulphate .....	80H <sub>2</sub> O	1·06401	71·819	71·82	63·500	63·50	60·992	60·99	1·1776
	240H <sub>2</sub> O	1·02857	73·028	73·03	64·557	64·56	62·041	62·04	1·1771
	—	1·19321	76·991	76·99	68·095	68·09	65·307	65·30	1·1790
	—	1·19321	76·992	76·99	68·076	68·09	65·295	65·30	1·1790
Potassium nitrate .....	40H <sub>2</sub> O	1·12274	77·476	77·45	68·557	68·54	65·754	65·74	1·1781
	—	1·12800	77·431	77·45	68·531	68·54	65·729	65·74	1·1781
	80H <sub>2</sub> O	1·08951	77·698	77·69	68·791	68·80	65·871	65·87	1·1794
	120H <sub>2</sub> O	1·06952	77·698	77·69	68·804	68·80	65·871	65·87	1·1794
Potassium bromide .....	—	1·07020	77·824	77·82	68·921	68·92	66·085	66·04	1·1764
	—	1·14747	77·813	77·81	68·887	68·83	66·049	66·05	1·1783
	—	1·14761	77·804	77·81	68·839	68·83	66·048	66·05	1·1783
	40H <sub>2</sub> O	1·08859	78·081	78·08	68·839	68·83	66·048	66·05	1·1783
Potassium bromide .....	80H <sub>2</sub> O	1·06813	78·102	78·10	68·839	68·83	66·048	66·05	1·1783
	120H <sub>2</sub> O	1·06321	78·198	78·19	68·839	68·83	66·048	66·05	1·1783
	—	1·16609	77·089	77·05	68·164	68·17	65·387	65·38	1·1785
	—	1·16610	77·087	77·05	68·169	68·17	65·388	65·38	1·1785
Potassium bromide .....	40H <sub>2</sub> O	1·10608	77·581	77·58	68·169	68·17	65·387	65·38	1·1785
	80H <sub>2</sub> O	1·07640	77·790	77·79	68·169	68·17	65·387	65·38	1·1785
	120H <sub>2</sub> O	1·05975	77·947	77·96	68·169	68·17	65·387	65·38	1·1785
	—	1·05975	77·947	77·96	68·169	68·17	65·387	65·38	1·1785

Table XII.—Volume and Conductivity Changes in Mixed Solutions of Sugar and Salts at Various Dilutions. One gramme-molecule of salt dissolved in 1000 grammes of water + 0, 40, 80 or 120 gramme-molecules of water, with and without 1 gramme-molecule of sugar.

Solute.	Extra water.	Density of solutions.	Volume of solutions in c.c.	$[V_{Aq} + E - V_{Aq}]$ , in c.c.	$[V_{Aq} + E + Sg - V_{Aq} + Sg]$ , in c.c.	$[B - A]$ in c.c.	Molecular conductivity of salt.	Loss in conductivity per cent.
NaCl .....	—	1·08016	1021·56	18·58	20·12	+1·54	85·91	44·6
NaCl + sugar .....	—	1·13340	1235·80	18·35	19·23	+0·88	91·85	29·3
NaCl .....	40H <sub>2</sub> O	1·02009	1743·47	18·08	18·85	+0·77	64·98	21·6
NaCl + sugar .....	40H <sub>2</sub> O	1·08394	1956·44	17·95	18·68	+0·73	96·31	17·2
NaCl .....	80H <sub>2</sub> O	1·01345	2465·35	6·66	6·76	+3·89	74·71	51·5
NaCl + sugar .....	80H <sub>2</sub> O	1·06066	2678·20	4·47	4·75	+2·29	97·97	33·9
NaCl .....	120H <sub>2</sub> O	1·00377	3187·36	3·11	3·99	+1·64	80·74	25·4
NaCl + sugar .....	120H <sub>2</sub> O	1·04729	3399·96	2·28	3·09	+1·71	53·24	20·7
MgSO <sub>4</sub> .....	—	1·10872	1009·64	40·50	42·02	+1·52	61·07	43·7
MgSO <sub>4</sub> + sugar .....	—	1·19323	1225·73	39·96	41·00	+1·04	92·84	29·2
MgSO <sub>4</sub> .....	40H <sub>2</sub> O	1·06408	1729·59	39·68	40·09	+0·41	100·61	21·7
MgSO <sub>4</sub> + sugar .....	40H <sub>2</sub> O	1·12274	1943·87	39·31	40·02	+0·71	71·28	17·1
MgSO <sub>4</sub> .....	80H <sub>2</sub> O	1·04491	2450·88	36·09	37·49	+1·40	115·55	45·1
MgSO <sub>4</sub> + sugar .....	80H <sub>2</sub> O	1·08946	2664·10	35·67	36·65	+0·98	63·46	30·0
MgSO <sub>4</sub> .....	120H <sub>2</sub> O	1·03428	3171·69	35·52	36·00	+0·48	119·88	22·3
MgSO <sub>4</sub> + sugar .....	120H <sub>2</sub> O	1·07010	3385·27	35·42	35·82	+0·40	121·90	17·6
KNO <sub>3</sub> .....	—	1·05531	1043·48	1089·07	1089·07	—	108·07	—
KNO <sub>3</sub> + sugar .....	—	1·14761	1257·70	1253·17	1253·17	—	89·59	—
KNO <sub>3</sub> .....	40H <sub>2</sub> O	1·03179	1765·08	1760·79	1760·79	—	115·55	—
KNO <sub>3</sub> + sugar .....	40H <sub>2</sub> O	1·09359	1978·21	1973·86	1973·86	—	63·46	—
KNO <sub>3</sub> .....	80H <sub>2</sub> O	1·02181	2496·95	2482·79	2482·79	—	119·88	—
KNO <sub>3</sub> + sugar .....	80H <sub>2</sub> O	1·06813	2699·44	2695·35	2695·35	—	83·88	—
KNO <sub>3</sub> .....	120H <sub>2</sub> O	1·01635	3208·72	3204·82	3204·82	—	121·90	—
KNO <sub>3</sub> + sugar .....	120H <sub>2</sub> O	1·05321	3421·30	3417·10	3417·10	—	94·75	—
KBr .....	—	1·07703	1089·07	1089·07	1089·07	—	101·88	—
KBr + sugar .....	—	1·16607	1253·17	1253·17	1253·17	—	115·55	—
KBr .....	40H <sub>2</sub> O	1·04448	1760·79	1760·79	1760·79	—	63·46	—
KBr + sugar .....	40H <sub>2</sub> O	1·10608	1973·86	1973·86	1973·86	—	119·88	—
KBr .....	80H <sub>2</sub> O	1·03074	2482·79	2482·79	2482·79	—	83·88	—
KBr + sugar .....	80H <sub>2</sub> O	1·07640	2695·35	2695·35	2695·35	—	121·90	—
KBr .....	120H <sub>2</sub> O	1·02318	3204·82	3204·82	3204·82	—	94·75	—
KBr + sugar .....	120H <sub>2</sub> O	1·05975	3417·10	3417·10	3417·10	—	101·88	—

*An Electrical Method of Counting the Number of  $\alpha$ -Particles from Radio-active Substances.*

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The total number of  $\alpha$ -particles expelled per second from 1 gramme of radium has been estimated by Rutherford\* by measuring the charge carried by the  $\alpha$ -particles expelled from a known quantity of radium in the form of a thin film. On the assumption that each  $\alpha$ -particle carries the ionic charge  $e = 3.4 \times 10^{-10}$  electrostatic unit, it was shown that  $6.2 \times 10^{10}$   $\alpha$ -particles are expelled per second from 1 gramme of radium itself, and four times this number when in radio-active equilibrium with its three  $\alpha$ -ray products, viz., the emanation, radium A and C. In order to reconcile the value of  $e/m$  found for the  $\alpha$ -particle with that to be expected for the helium atom, it was later† pointed out that the  $\alpha$ -particle should carry a charge equal to  $2e$ . On this assumption, the number of  $\alpha$ -particles expelled per second per gramme of radium is reduced to one-half the first estimate.

The need of a method of counting the  $\alpha$ -particles directly without any assumption of the charge carried by each has long been felt, in order to determine the magnitude of the various radio-active quantities with a minimum amount of assumption. If the number of  $\alpha$ -particles expelled from a definite quantity of radio-active matter could be determined by a direct method, the charge carried by each particle could be at once known by measuring the total positive charge carried by the  $\alpha$ -particles. In this way, it should be possible to throw some light on the question whether the  $\alpha$ -particle carries a charge  $e$  or  $2e$ , and thus settle the most pressing problem in radio-activity, viz., whether the  $\alpha$ -particle is an atom of helium.

In considering a possible method of counting the number of  $\alpha$ -particles, their well-known property of producing scintillations in a preparation of phosphorescent zinc sulphide at once suggests itself. With the aid of a microscope, it is not very difficult to count the number of scintillations appearing per second on a screen of known area when exposed to a source of  $\alpha$ -rays. The doubt, however, at once arises whether every  $\alpha$ -particle produces a scintillation, for it is difficult to be certain that the zinc sulphide is homogeneous throughout. No confidence can be placed in such a method of

\* 'Phil. Mag.,' August, 1905.

† Rutherford, 'Phil. Mag.,' October, 1906.

counting the total number of  $\alpha$ -particles (except as a minimum estimate), until it can be shown that the number so obtained is in agreement with that determined by some other independent method which does not involve such obvious uncertainties. The results of some observations on the number of scintillations produced by the  $\alpha$ -particles from radium will be discussed later.

It has been recognised for several years that it should be possible by refined methods to detect a single  $\alpha$ -particle by measuring the ionisation it produces in its path. On the assumption that an  $\alpha$ -particle carries an ionic charge  $e$ , one of us has shown that the  $\alpha$ -particle expelled from radium itself produces 86,000 ions in its path in air before it is stopped. Taking the charge of an  $\alpha$ -particle as  $2e$ , this number is reduced to one-half. Consequently if the  $\alpha$ -particle passes through air in a strong electric field, the total quantity of electricity transferred to the electrodes is  $43,000e$ . Taking  $e = 3.4 \times 10^{-10}$  E.S. unit, this corresponds to  $1.46 \times 10^{-5}$  E.S. unit. For the purpose of illustration, suppose that a Dolezalek electrometer of capacity 50 E.S. units, which has a sensibility of 10,000 mm. divisions per volt between the quadrants, is used for detection of the ionisation. The quantity  $1.46 \times 10^{-5}$  unit transferred to the electrometer system would cause a deflection of the needle of 0.3 mm. This is small but detectable. In a similar way, if an electroscope of capacity 2 E.S. units be employed instead of an electrometer, the movement of the leaf would correspond to a difference of potential of  $2.1 \times 10^{-3}$  volt. While there is no inherent impossibility in detecting such small quantities of electricity by either the electroscope or electrometer, yet the measurement would have to be of a refined character in order to get rid completely of all extraneous sources of disturbance. One difficulty is that the moving system in very sensitive electrometers or electroscopes has a long period of swing and consequently moves very tardily when a small difference of potential is suddenly applied. Some preliminary experiments to detect a single  $\alpha$ -particle by its direct ionisation were made by us, using specially constructed sensitive electroscopes. As far as our experience has gone, the development of a certain and satisfactory method of counting the  $\alpha$ -particles by their small direct electrical effect is beset with numerous difficulties.

We then had recourse to a method of automatically magnifying the electrical effect due to a single  $\alpha$ -particle. For this purpose we employed the principle of production of fresh ions by collision. In a series of papers, Townsend\* has worked out the conditions under which ions can be produced by collisions with the neutral gas molecules in a strong electric field. The

\* 'Phil. Mag.,' February, 1901 ; June, 1902 ; April, 1903 ; September and November, 1903.

effect is best shown in gases at a pressure of several millimetres of mercury. Suppose that the current between two parallel plates immersed in a gas at low pressure is observed when the air is ionised by X-rays. The current through the gas for small voltages at first increases with the field and then reaches a saturation value, as is ordinarily observed in ionised gases at atmospheric pressure. When the field is increased beyond a certain value, however, the current rises rapidly. Townsend has shown that this effect is due to the production of fresh ions in the gas by the collision of the negative ions with the gas molecules. At a later stage, when the electric field approaches the value required to cause a spark, the positive ions also become effective as ionisers but to a much smaller degree than the negative. Under such conditions, the small current through the gas due to the external ionising agency may be easily increased several hundred times. The magnification of the current depends upon the voltage applied and becomes very large just below the sparking value.

In our experiments to detect a single  $\alpha$ -particle, it was arranged that the  $\alpha$ -particles could be fired through a gas at low pressure exposed to an electric field somewhat below the sparking value. In this way, the small ionisation produced by one  $\alpha$ -particle in passing along the gas could be magnified several thousand times. The sudden current through the gas due to the entrance of an  $\alpha$ -particle in the testing vessel was thus increased sufficiently to give an easily measurable movement of the needle of an ordinary electrometer.

*Experimental Arrangement.*—Before considering the various difficulties that arose in the course of the investigations, a brief description will be given of the method finally adopted. The experimental arrangement is shown in fig. 1. The detecting vessel consisted of a brass cylinder A, from 15 to

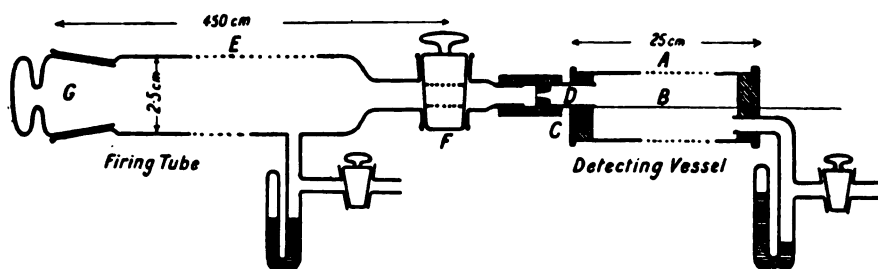


FIG. 1.

25 cm. in length, 1.7 cm. internal diameter, with a central insulated wire B passing through ebonite corks at the ends. The wire B was in most experiments of diameter 0.45 mm. The cylinder, with a pressure gauge attached,



was exhausted to a pressure of from 2 to 5 cm. of mercury. The central wire was connected with one pair of quadrants of a Dolezalek electrometer and the outside tube to the *negative*\* terminal of a large battery of small accumulators, the other pole of which was earthed. In the ebonite cork C was fixed a short glass tube D of internal diameter 5 mm., in the end of which was a circular opening of about 1.5 mm. diameter. This opening, through which the  $\alpha$ -particles entered the testing vessel, was covered with a thin sheet of mica tightly waxed over the end of the tube. In most experiments the thickness of mica was equivalent, as regards stopping power of the  $\alpha$ -particle, to about 5 mm. of air at atmospheric pressure. Over the tube D was fixed a wide rubber tube, to the other end of which was attached a long glass tube E of 450 cm. in length and 2.5 cm. diameter. A large stop-cock F with an opening 1 cm. in diameter was attached to the end of the glass tube next to the detecting vessel. The other end of the long glass tube was closed by a ground stopper G.

The general procedure of an experiment was as follows. The voltage applied to the testing vessel was adjusted so that the ionisation in the vessel due to an external source of  $\gamma$ -rays was increased by collision several thousand times. The radium tube which served as a source of  $\gamma$ -rays was then removed. Under ordinary conditions, when all external sources of ionisation were absent, there was always a small current passing through the gas. In order to avoid the steady movement of the electrometer needle due to this cause, the current was allowed to leak away through a radio-active resistance attached to the electrometer system. This consisted of two insulated parallel plates, the upper connected with the electrometer and the lower with earth. A layer of radio-active material was placed on the lower plate. As the potential of the electrometer needle rose, equilibrium was soon reached between the current supplied to the electrometer and that which leaked away due to the ionised gas between the plates. This arrangement was of great importance to the success of the experiments, for it practically served to eliminate disturbances due to electrostatic effects or to slow changes in the E.M.F. of the battery. Any sudden rise of potential of the electrometer, for example that due to the entrance of an  $\alpha$ -particle in the detecting vessel, then manifested itself as a sudden *ballistic* throw of the electrometer needle. The charge rapidly leaked away and in a few seconds the needle was again at rest in its old position.

The active matter, in the form of a thin film of not more than 1 square cm.

\* If the tube were connected to the positive pole of the battery, the magnification by collision only became appreciable near the sparking voltage. With the negative pole, the magnification increased more gradually and was far more under control.

in area, was fixed in one end of a hollow soft iron cylinder which could be moved along the glass tube from the outside by means of an electro-magnet. The glass tube was then exhausted by means of a Fleuss pump and, if required, to a still lower pressure by means of a tube of cocoanut charcoal immersed in liquid air.

When the stop-cock was closed, no  $\alpha$ -particles could enter the vessel, and the steadiness of the electrometer needle could thus be tested at intervals during an experiment. On opening the stop-cock, a small fraction of the total number of  $\alpha$ -particles expelled per second passed through the aperture into the detecting vessel. In practice, it was found convenient to arrange the intensity of the active matter and its distance from the opening so that from three to five  $\alpha$ -particles entered the detecting vessel per minute. It became difficult to count a number greater than this with certainty, since the needle had not time to come to rest between successive throws.

The following example serves to illustrate the character of the observations. The source of  $\alpha$ -rays in this case was a metal plate about 0.5 square cm. in area made active by exposure for several hours in a large quantity of radium emanation. Fifteen minutes after removal from the emanation, the  $\alpha$ -radiation from the plate is due almost entirely to radium C. The active matter is in the form of a thin film, so that all the  $\alpha$ -particles are expelled with the same velocity. The intensity of the radiation from radium C decreases with time, falling to half value about one hour after removal and later at a more rapid rate. In this particular case, the detecting tube was filled with carbon dioxide to a pressure of 4.2 cm. The E.M.F. applied was 1320 volts. The active plate was at a distance of 350 cm. from the aperture, which was of diameter 1.23 mm. Observations of the number and magnitude of the throws due to the  $\alpha$ -particles were continued over an interval of 10 minutes. The results are shown in the following table:—

	Number of throws.	Magnitude of successive throws in scale divisions.
1st minute .....	4	11, 12, 10, 11
2nd " .....	3	10, 11, 8
3rd " .....	5	10, 9, 13, 8, 12
4th " .....	4	18,* 8, 12
5th " .....	3	10, 6, 10
6th " .....	4	9, 10, 12, 11
7th " .....	2	10, 11
8th " .....	3	11, 13, 8
9th " .....	3	8, 20*
10th " .....	4	8, 12, 14, 6
Average per minute = 3.5		Average throw = 10 divisions.

Each scale division was equal to 2.5 mm. The intensity of the  $\alpha$ -radiation decreased about 15 per cent. during the time of observation.

When the stop-cock was closed so that no  $\alpha$ -particles could enter the detecting vessel, the electrometer needle was very steady, the maximum excursion of the needle from the zero position in the course of 10 minutes being not more than three scale divisions. Only two or three excursions of such amplitude occurred in that interval. We see from the table that the average throw observed with the stop-cock open was 10 divisions.\* All small excursions of magnitude less than three scale divisions are omitted. With the exception of the two numbers marked with asterisks, each of the throws given in the table is due to a single  $\alpha$ -particle. The two large throws marked with asterisks are each due to the superposition of the separate effects due to two successive  $\alpha$ -particles entering the detecting vessel within a few seconds of each other. This was readily seen from the peculiarity of the motion of the spot of light on the scale. As the electrometer needle was moving slowly near the end of its swing caused by the effect of one  $\alpha$ -particle, a second impulse due to the entrance of another was communicated to it, and caused it to move again more rapidly. Such double throws occur occasionally, and are readily recognised, provided the interval between the entrance of successive  $\alpha$ -particles is not less than one second.

It will be noted that the number of  $\alpha$ -particles entering the opening per minute, and also the interval between successive throws varied within comparatively wide limits. Such a result is to be anticipated on the theory of probability. We may regard a constant source of  $\alpha$ -rays as firing off  $\alpha$ -particles equally in all directions at a nearly constant rate. The number per minute fired through a small opening some distance away is on the average constant if a large number of throws are counted. When only a small number of throws are observed over a short interval, the number is subject to considerable fluctuations, the probable percentage departure of the observed number from the correct average being greater the smaller the number of  $\alpha$ -particles entering within a given time. This phase of the subject is of considerable interest and importance, and will be discussed in more detail later in the paper. It suffices here to say that the variation of the observed number per minute is well within the limits to be anticipated on the general laws of probability.

It is seen that the throws due to an  $\alpha$ -particle are somewhat variable in magnitude. Such a result is to be anticipated for several reasons. In the first place, the  $\alpha$ -particles do not all pass along the detecting tube at the same

\* The magnitude of the throw due to a single  $\alpha$ -particle is dependent upon the E.M.F. applied, and can be varied over wide limits.

distance from the axis. The magnification of the ionisation is less for those that pass closest to the central wire. In addition, as will be shown later, there is always a scattering of the  $\alpha$ -rays by the mica screen and by the gas in the detecting vessel. This tends to spread out the pencil of rays in the detecting vessel, and consequently to introduce still greater differences in the effects due to individual  $\alpha$ -particles.

*Detection of  $\alpha$ -Particles from Uranium, Thorium, Radium, and Actinium.*

The throws of the electrometer observed with the stop-cock open have been ascribed to the  $\alpha$ -particles fired into the detecting vessel. This can be readily proved by placing a thin screen between the source of radiation and the detecting vessel. The throws of the electrometer disappear if this screen, together with the mica plate covering the hole, is of the right thickness to stop the  $\alpha$ -particles entirely. Under ordinary conditions, the effect due to a  $\beta$ -particle is very small compared to that due to an  $\alpha$ -particle, and is not detectable. If a plate coated with the active deposit of radium is used as a source of radiation, it is found that the decay curve obtained by counting the  $\alpha$ -particles emitted agrees closely with the ordinary  $\alpha$ -ray decay curve.

By this electrical method, we have detected the expulsion of  $\alpha$ -particles not only from radium and its products but also from uranium, thorium, and actinium. For example, a plate, made active by exposure to the emanation of a preparation of actinium, gave effects in the testing vessel due to an  $\alpha$ -particle of about the same magnitude as that due to an  $\alpha$ -particle from radium C. The decay curve obtained by counting the  $\alpha$ -particles agreed closely with the known curve. A thin film of radium itself showed a similar effect. As the activity rose, consequent upon the production of fresh emanation and its occlusion in the radium, the number of  $\alpha$ -particles entering the detecting vessel increased.

A special apparatus (see fig. 2) was used to detect the emission of  $\alpha$ -particles from weak radio-active substances like uranium and thorium.

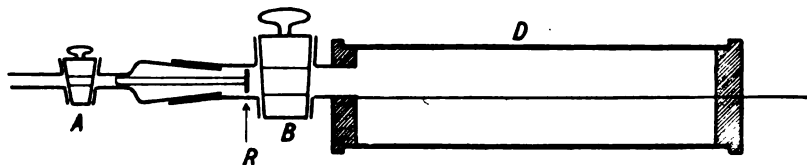


FIG. 2.

The active matter spread on a plate R (fig. 2) was placed about 5 cm. from the opening, which in this case was about 1 cm. diameter, and without any mica screen. A stop-cock of wide bore was placed between the active matter

and the testing vessel D. With the stop-cock closed, the electrometer needle was very steady. On opening the stop-cock, about two throws per minute of the ordinary magnitude due to an  $\alpha$ -particle were observed from the uranium. This was about the number to be expected from known data.

It may be of interest to record an experiment made with a preparation of thorium hydroxide. A small quantity of this (about 3. milligrammes) was wrapped in thin paper, which stopped the  $\alpha$ -rays but allowed the emanation to pass through freely. On opening the stop-cock, the emanation diffused into the detecting vessel and immediately a large deflection of the electrometer was observed. After a few minutes an approximately steady radio-active state was reached. The electrometer needle, however, never remained steady, but made wide oscillations on either side of the mean position. Such an effect was to be anticipated, for when occasionally two or three  $\alpha$ -particles from the emanation were fired along the cylinder within a second or two of each other, the electrometer needle was widely deflected. When the stop-cock was closed, the mean deflection due to the emanation in the testing vessel decreased with the time at the rate characteristic of the thorium emanation, but the electrometer needle continued to give excursions to and fro until the activity of the emanation had disappeared.

There is no doubt that the principle of automatic increase of the ionisation by collision can be used to extend considerably the range of measurement of minute quantities of radio-active matter.

#### *Experimental Difficulties.*

The final type of detecting cylinder which was found most satisfactory for counting purposes was of small diameter, viz., 1.7 cm., and of length not more than 25 cm. We shall now discuss the reasons that led us to adopt such a small detecting vessel. In the preliminary experiments, a cylinder of diameter 3.5 cm. and length 1 metre was used. With a pressure of air of 4 cm., the ionisation and stopping power of an  $\alpha$ -particle passing the length of the cylinder was equivalent to that due to traversing 5.3 cm. of air at atmospheric pressure. Since the mica screen had a stopping power equal to only 5 mm. of air, an  $\alpha$ -particle from radium C (range 7 cm.) produced the major part of its total ionisation in the detecting cylinder. Using such a vessel, it was not difficult to adjust the voltage so that an  $\alpha$ -particle entering the vessel produced a throw of at least 100 mm. of the electrometer scale. Under such conditions, however, it was found impossible to avoid natural disturbances of the electrometer needle, when the stop-cock was closed, which were comparable in magnitude and character with those due to the entrance of an  $\alpha$ -particle. These sudden movements of the electrometer needle were not numerous, but

were sufficient to interfere with an accurate counting of the number of  $\alpha$ -particles. These disturbances were inherent in the vessel and could not be got rid of by changing the pressure or nature of the gas or the diameter of the central wire. There is no doubt these irregular movements of the electrometer needle must be ascribed to a slight natural radio-activity of the walls of the brass tube. An  $\alpha$ -particle projected near the end of the tube in the direction of the axis of the tube would produce a throw of the electrometer needle of about the same magnitude as that due to an  $\alpha$ -particle fired through the opening parallel to the axis of the tube. The great majority of the  $\alpha$ -particles emitted by the tube will only travel a short distance before being stopped by the walls, and consequently will only give rise to small individual movements of the needle. The greater part of the current observed by the electrometer with the aperture closed was due to this natural ionisation increased several thousand times by the agency of the strong electric field. The correctness of this conclusion was borne out by the observation that any change of the applied voltage, and consequently of the magnification, altered the magnitude of the natural disturbances, and the throw due to an  $\alpha$ -particle in about the same ratio. In addition, it was observed that the number of the natural disturbances fell off rapidly with decrease of the diameter of the detecting tube. For example, the natural movements of the electrometer needle, using a long tube of 5 cm. diameter, were so numerous and so vigorous that it was impossible to use it for counting  $\alpha$ -particles at all. With a tube, however, of 1.7 cm. diameter, the natural movements were very occasional, and of magnitude small compared with the effect due to an  $\alpha$ -particle. Such a rapid decrease of the disturbances is to be anticipated in the light of the above explanation. If tubes are taken of the same length and of the same natural radio-activity per unit area, but of different diameters, the total number of  $\alpha$ -particles shot out is proportional to their radii. Taking corresponding cross sections of the tubes, the fraction of the total number of  $\alpha$ -particles emitted, which travel to the end of the tubes without striking the walls, is proportional to the cross sectional area of the tubes. Consequently the number of  $\alpha$ -particles which pass along the tube without being stopped by the walls varies directly as the cube of the radius. We thus see that the sudden large movements of the electrometer needle due to the radio-activity of the walls should fall off very rapidly with decrease of the diameter—a result in harmony with the experimental observations.

Since the electrical capacity of the detecting vessel was smaller than the electrometer and its connections, it seemed advisable at first to use long detecting tubes in order to make the ionisation in it due to an  $\alpha$ -particle as large as possible. From lack of accumulators at our command, it was not

found feasible to work at a higher pressure than about 6 cm. of mercury, for at this pressure about 1500 volts were necessary to obtain the requisite magnification. Experiments were consequently made with a tube 135 cm. long, of diameter 1.7 cm., with a gas pressure varying from 2 to 6 cm. The natural disturbances of the electrometer needle in this vessel were very small, and it was found possible to increase the magnification such that an  $\alpha$ -particle produced a throw of several hundred millimetre divisions on the scale. The throws due to successive  $\alpha$ -particles were, however, very variable in magnitude. This is illustrated by the following table of observations:—

Air pressure, 3 cm.; radium C. Source of radiation; distance from aperture, 350 cm.

	Number of $\alpha$ -particles.	Magnitude of successive throws.
1st minute ...	4	6, 7, 10, 16
2nd " ...	2	21, 15
3rd " ...	1	36
4th " ...	4	6, 25, 17, 11
5th " ...	4	4, 28, 13, 13
6th " ...	5	9, 16, 7, 6, 24

The great difference in the magnitude of the throws could not be ascribed to several particles entering together, for similar divergences were noted when on an average only one  $\alpha$ -particle entered the detecting vessel per minute. Special experiments were made with sources of radiation of small area at a distance of 4 metres from the aperture and with a small aperture in the detecting vessel. Under such conditions, it was arranged that if the  $\alpha$ -particles travelled in straight lines, they should strike the end of the detecting tube within an area of 1 square mm. The use of such a theoretically narrow pencil of rays had no effect, however, in equalising the magnitude of the throws. Finally, after a series of experiments, it was found that this effect was due to the *scattering of the  $\alpha$ -particles in their passage through the mica screen and through the gas in the detecting vessel*. In a previous paper by one of us,\* attention had been directed to the undoubted scattering of the  $\alpha$ -particles in their passage through matter, and the magnitude of this scattering had been determined by the photographic method in special cases. We did not at first realise the importance of this effect in our experimental arrangement. Some of the  $\alpha$ -particles, in passing through the thin sheet of mica, are deflected from their rectilinear path, and this deflection

\* Rutherford, 'Phil. Mag.', August, 1906.

is continued in their passage along the gas of the tube. The scattering was sufficiently great to cause a large fraction of the  $\alpha$ -particles to impinge on the walls of the tube. The small throws observed were due to  $\alpha$ -particles which only traversed a small fraction of the length of the tube before being stopped, while the largest throws were due to those that passed along the tube without striking the walls. A special series of experiments by a new method were made by one of us\* to determine the magnitude of this scattering in special cases. An account of these experiments will be published in a separate paper.

As it was not feasible to decrease the scattering by reducing the thickness of the mica screen over the opening, the only way of making the throws more uniform was to diminish the length of the tube. It was for this reason that a tube only 25 cm. long was used. In this short distance, the  $\alpha$ -particles were not deflected sufficiently to strike the walls of the tube, and the great majority travelled the whole length of the detecting vessel. Under these conditions, the throws of the electrometer due to the  $\alpha$ -particles at once became far more uniform. An example of the throws obtained in the short vessel is given in Table I, p. 145. In the long detecting tube, there was a tendency to overlook the small throws and thus to underestimate the number of  $\alpha$ -particles entering into the detecting vessel. The presence of this scattering also makes it necessary to exhaust the long firing tube to a low pressure. The presence of gas in this tube tends to deflect the  $\alpha$ -particles from their rectilinear path and, if the tube is narrow near the aperture, to reduce the number entering the detecting vessel. Such a decrease of the number was at once observed, if the pressure of the gas in the long tube were raised so that its stopping power was equivalent to 2 or 3 cm. of air at atmospheric pressure.

#### *The Number of $\alpha$ -Particles expelled from Radium.*

A series of experiments was made to determine as accurately as possible by the electrical method the number of  $\alpha$ -particles expelled per second from 1 gramme of radium. The arrangement of the apparatus was similar to that shown in fig. 1. A source of homogeneous  $\alpha$ -rays was placed at a convenient distance from the detecting vessel in the firing tube, and the average number of  $\alpha$ -particles entering the aperture per minute was determined by counting the throws of the electrometer needle.

Let  $Q$  be the average number of  $\alpha$ -particles expelled per second from the source, consisting of a thin film of active matter. Let  $A$  be the area in

\* See accompanying paper by H. Geiger, "Scattering of the  $\alpha$ -Particles by Matter," p. 174, *infra*.



square cm. of the aperture in the detecting vessel, and  $r$  the distance in centimetres of the source of rays from the aperture. It was verified experimentally that the  $\alpha$ -particles on an average are projected equally in all directions. Consequently, the fraction of the total number of  $\alpha$ -particles expelled from the source which enter the detecting vessel is equal to the area of the aperture divided by the area of the surface of a sphere of radius equal to the distance of the source from the opening. The average number  $n$  of  $\alpha$ -particles entering the opening per second is thus given by

$$n = \frac{QA}{4\pi r^2}. \quad (1)$$

This expression holds for all distributions of active matter of dimensions small compared with the distance  $r$ , provided that each element of surface of the source can fire directly into the aperture. In practice, the active matter is usually spread on the surface of a body of sufficient thickness to stop the  $\alpha$ -particles fired into it, so that only half the total number of  $\alpha$ -particles escape from its surface. This in no way interferes with the correctness of the above expression for the number.

After some preliminary experiments with thin films of radium itself, it was decided to employ radium C as a source of  $\alpha$ -rays in the counting experiments. If a body is exposed for about three hours in the presence of the radium emanation, the activity imparted to it reaches a maximum value. Fifteen minutes after removal of the body from the emanation, the radiation due to radium A has practically disappeared, and the  $\alpha$ -radiation is then due entirely to radium C. Under these conditions all the  $\alpha$ -particles escape with the same velocity, and have a range in air of 7 cm. The use of radium C has numerous advantages. The active deposit is in the form of an extremely thin film, and the amount of active matter deposited on a body can readily be varied by altering the amount of emanation or the surface exposed to it. The chief advantage, however, lies in the ease and certainty of measurement of the quantity of active matter present in terms of the radium standard.\* The penetrating  $\gamma$ -rays from radium in equilibrium arise entirely from its product, radium C. Consequently, by comparing the  $\gamma$ -ray activity of the active deposit with the radium standard, the amount of radium C present may be expressed in terms of the quantity of radium C in equilibrium with 1 gramme of radium. The chief disadvantage lies in the fact that the activity due to radium C rapidly diminishes, falling to half value in about one hour and to 14 per cent. of the maximum in two hours.

\* The radium standard employed in these experiments is one that has been in use for several years. It is a part of a sample of radium which gave a heating effect of 110 gramme-calories per hour per gramme.

The shape of the body made active by exposure to the emanation must be such that each element of the active surface, when in position in the firing tube, must be in full view of the aperture of the detecting vessel. Examples of the surfaces employed are shown in fig. 3: *a* and *b* are of glass, and *c* a

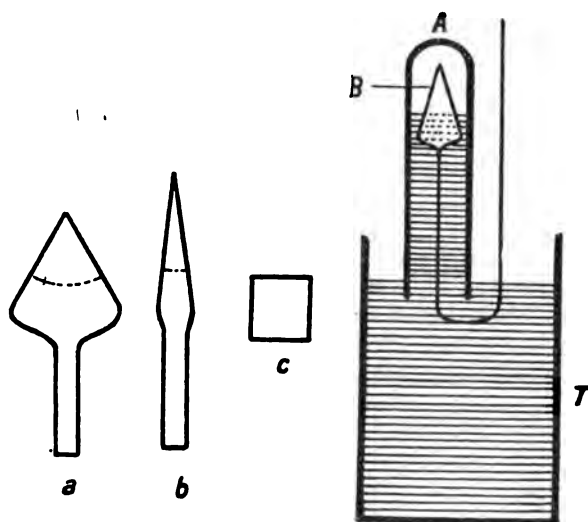


FIG. 3.

plane sheet of glass or iron, the dotted lines representing the lower limit of the active matter. The emanation, mixed with 1 or 2 c.c. of air, was collected over mercury in the end of the tube A (fig. 3). The body B, to be made active, was fixed to a glass U-tube, and introduced into the emanation space by means of the mercury trough T. After remaining in position for an interval of not less than three hours, the active body was removed and immediately tested in terms of the radium standard, using a fixed  $\gamma$ -ray electroscope. The active source was then placed in position in the firing tube, which was exhausted to a low pressure. In order to follow the changes of activity of the source, a second travelling  $\gamma$ -ray electroscope was employed in which the activity of the source was determined *in situ*. In the counting experiments the active body, as it diminished in activity, was moved nearer the detecting vessel. The electroscope was moved so as to be always directly over the active body and always at the same distance from it. At the end of the counting experiments, the active body was removed from the firing tube and its  $\gamma$ -ray activity again determined on the fixed electroscope. In this way a complete check was obtained on the activity measurements as well as a direct determination of the decay curve of the active body.

The general procedure of an experiment was as follows. After the  $\gamma$ -ray activity had been accurately measured, observations of the number of throws were made continuously for an interval of 10 minutes. The  $\gamma$ -ray activity was then determined again, and then another 10 minutes' count, and so on. When the number of  $\alpha$ -particles entering the opening had fallen to between one and two per minute, the active body was brought nearer the opening, and observations continued as before over a total interval of about two hours.

The following table illustrates the results obtained with the same source as it decayed in activity. The detecting vessel contained air at a pressure of 3.75 cm. and about 1200 volts were applied. The diameter of the aperture was 1.23 mm.

Distance of active body from aperture.	Mean $\gamma$ -ray activity of source.	Number of throws observed in 10 mins.	Number of $\alpha$ -particles expelled per gramme.
350 cm.	0.309 mgr. Ra	45	$3.06 \times 10^{10}$
350 "	0.154 "	25	$3.33 \times 10^{10}$
350 "	0.11 "	16	$2.96 \times 10^{10}$
150 "	0.055 "	49	$3.43 \times 10^{10}$
150 "	0.081 "	25	$3.11 \times 10^{10}$

Total number of throws = 160. Average =  $3.18 \times 10^{10}$ .

The second column gives the mean  $\gamma$ -ray activity of the source in terms of milligrammes of pure radium in equilibrium. The fourth column gives the total number of  $\alpha$ -particles from radium C expelled per second in 1 gramme of radium in equilibrium. This number is calculated as follows. We have shown (equation 1) that the total number of  $\alpha$ -particles  $Q$  emitted per second by the source is given by

$$Q = \frac{4\pi r^2}{A} \cdot n.$$

The total number  $Q_0$  expelled for a  $\gamma$ -ray activity corresponding to 1 gramme of radium is given by

$$Q_0 = \frac{Q}{\rho} = \frac{4\pi r^2}{A} \cdot \frac{n}{\rho},$$

where  $\rho$  is the  $\gamma$ -ray activity of the source in terms of 1 gramme of radium. Since  $n$  and  $\rho$  are determined experimentally, and  $r$  and  $A$  are known, the value of  $Q_0$  can be at once calculated. The calculated values of  $Q_0$  for each experiment are given in the fourth column, and serve as a comparison of the agreement for the different observations.\* The value of  $4\pi r^2/A$  for the first

\* On account of the probability variation, it is not to be expected that the numbers in the fourth column should agree very closely.

three experiments at a distance of 350 cm. is equal to  $1.25 \times 10^8$ , *i.e.*, on an average, out of 125,000,000  $\alpha$ -particles fired from the source, only one passes through the aperture.

In the course of our experiments, we have verified, as far as possible, the correctness of the assumptions on which the deduction of the number of  $\alpha$ -particles expelled from 1 gramme of radium depends. These points are summarised below :—

(1) For a given intensity of radiation at a given distance, the average number of throws observed in the electrometer in a given interval is independent of the pressure or nature of the gas, and also of the magnification of the ionisation.

(2) The number of  $\alpha$ -particles entering the aperture is proportional to the activity of the source (measured by the  $\gamma$ -rays) and inversely proportional to the square of the distance of the source from the aperture over the range examined, *viz.*, from 375 to 100 cm.

(3) For a given intensity of radiation at a given distance, the number of  $\alpha$ -particles entering the detecting vessel is proportional to the area of the aperture.

(4) Using radium C as a source of rays, the  $\alpha$ -particles are, on an average, projected equally in all directions. This has been verified by observing that, within the limit of experimental error, the calculated number of  $\alpha$ -particles from radium C in 1 gramme of radium comes out the same whether the  $\alpha$ -particles entering the aperture escape nearly tangentially from the active surface, as in fig. 3, *b*, nearly normally, as in fig. 3, *c*, or at an intermediate angle, as in fig. 3, *a*.

The following table gives the results for a number of separate experiments. The average value of  $Q_0$  for each complete experiment, involving observations for different intensities of the source at different distances, is given in the last column.

Gas.	Pressure in detecting vessel.	Voltage.	Diameter of aperture.	Total number of throws counted.	Average value of $Q_0$ .
Air	3.75 cm.	1200 volts	1.23 mm.	161	$3.20 \times 10^{10}$
CO <sub>2</sub>	4.8 "	1360 "	1.23 "	59	$3.10 \times 10^{10}$
"	4.8 "	1360 "	1.23 "	118	$3.30 \times 10^{10}$
"	4.1 "	1240 "	1.23 "	93	$3.13 \times 10^{10}$
"	4.2 "	1320 "	1.92 "	194	$3.43 \times 10^{10}$
"	4.2 "	1320 "	1.92 "	150	$3.34 \times 10^{10}$
"	3.2 "	1320 "	1.92 "	99	$3.43 \times 10^{10}$
				Average =	$3.28 \times 10^{10}$

Except for the last experiment, in which a tube 21 cm. long and 2.4 cm. diameter was used, the detecting tube was of length 25 cm. and internal diameter 1.7 cm.

In determining the average value of  $Q_0$  given in the last column, which is itself an average of a large series of experiments, the weight to be assigned to each experiment of the series was taken as proportional to the number of  $\alpha$ -particles counted. It was found that this differed only slightly from the arithmetic mean. It is seen that the mean value of the collected observations for  $Q_0$  is  $3.28 \times 10^{10}$ . This is subject to a small correction for which it is difficult to assign a definite value. In order to make the throws due to an  $\alpha$ -particle as uniform as possible, it was arranged that the  $\alpha$ -particle passed obliquely across the detecting tube. A small fraction of the  $\alpha$ -particles entering the aperture would be stopped by the central wire, diameter 0.45 mm. In counting the number of  $\alpha$ -particles, there is a tendency to overlook or put down to natural disturbances all movements which are small compared with the average value. This would be the case if an  $\alpha$ -particle were stopped before travelling half the length of the tube. Taking into account the dimensions of the aperture, and of the copper wire and the scattering of the beam in its passage through the mica and the gas, it has been estimated that this correction cannot be more than 3 per cent. Making the correction, the value of  $Q_0$  becomes to the nearest figure  $3.4 \times 10^{10}$ .

We consequently conclude that, on an average,  $3.4 \times 10^{10}$   $\alpha$ -particles are expelled per second from the radium C present in 1 gramme of radium in equilibrium. From the experiments of Bragg, and the measurements by Boltwood of the ionisation due to the  $\alpha$ -particles from each of the products of radium, it appears certain that the same number of  $\alpha$ -particles are expelled per second from radium itself and from each of its  $\alpha$ -ray products in equilibrium with it.

It follows that 1 gramme of radium itself and each of its ray products in equilibrium with it expels  $3.4 \times 10^{10}$   $\alpha$ -particles per second. The total number of  $\alpha$ -particles emitted per second per gramme of radium in equilibrium with its three  $\alpha$ -ray products is  $13.6 \times 10^{10}$ . Taking as the simplest and most probable assumption that one atom of radium in breaking up emits one  $\alpha$ -particle, it follows that in 1 gramme of radium  $3.4 \times 10^{10}$  atoms break up per second.

#### *Counting of Scintillations.*

It is of importance to compare the number of scintillations produced on a zinc sulphide screen with the number of  $\alpha$ -particles counted by the electric method, in order to see whether each scintillation is due to a single  $\alpha$ -particle.

For this purpose the special zinc sulphide screens provided by Mr. F. H. Glew were used. A thin layer of zinc sulphide is spread over a thin glass plate, and the scintillations produced on the screen are readily seen through the glass by means of a microscope. In order to make the comparison as direct as possible, the same firing tube and aperture, covered with the mica screen, were used. The brass detecting tube was removed, and a small piece of zinc sulphide screen was attached to the end of the glass tube D (fig. 1), with its active surface towards the firing tube. Radium C served as a source of  $\alpha$ -rays, as in the electrical method.

Regener\* has made a number of observations upon the number of  $\alpha$ -particles expelled from an active preparation of polonium by the scintillation method. He has investigated the best conditions for viewing the scintillations and the relation between the focal lengths of the eye-piece and objective to obtain the maximum illumination due to each  $\alpha$ -particle. We have found his suggestions very useful in these experiments.

In our experiments a microscope of magnification 50 was used. The small area of screen, struck by the  $\alpha$ -particles, covered only about one-half of the field of view. The experiments were made at night in a dark room. As Regener suggests, it is advisable to illuminate the screen slightly by artificial light, in order to keep the eye focussed on the screen. The distance and intensity of the source were adjusted so that from 20 to 60 scintillations were observed per minute. It is difficult to continue counting for more than two minutes at a time, as the eye becomes fatigued. The zinc sulphide screen usually showed a few scintillations per minute with the stop-cock closed, due to natural radio-activity and other disturbances. These were counted before and after each experiment, and were subtracted from the number counted with the stop-cock open. It was usual to count 100 scintillations and to note the time with a stop-watch. The results of a series of observations for varying intensities of the radiations are given in the following table. The corrected number of scintillations observed per minute is given in Column ①. Taking  $3.4 \times 10^{10}$  as the number of  $\alpha$ -particles expelled per second per gramme, the calculated number of scintillations to be expected from the intensity of the radiation, if each  $\alpha$ -particle produces a scintillation, is given in Column 1. The ratio of the observed to the calculated number is given in Column 3.

\* 'Verh. d. D. Phys. Ges.,' vol. 10, p. 78, 1908.

Diameter of aperture, 1.23 mm. with mica covering. Distance of active source from aperture, 200 cm.

I. Calculated number of $\alpha$ -particles per minute.	II. Observed number of scintillations per minute.	III. Ratio of observed to calculated number.
39	31	0.80
38	49	1.29
34	29	0.85
32	31	0.97
31	32	1.03
28	27	0.96
27	28	1.04
25	21	0.84
23	25	1.09
21	21	1.00
Total number = 294		Average = 0.99

Another series of observations was made with a fresh piece of zinc sulphide screen with an aperture 3.02 times area of the first and without mica screen.

Calculated number of $\alpha$ -particles per minute.	Observed number of scintillations per minute.	Ratio of observed to calculated number.
36	31	0.86
34	30	0.88
31	31	1.00
30	29	0.97
27	29	1.07
Total number = 150		Average = 0.96

Considering the probability error, the agreement between the electrical and optical methods of counting is, no doubt, closer than one would expect. The result, however, brings out clearly that within the limit of experimental error, each  $\alpha$ -particle produces a scintillation on a properly prepared screen of zinc sulphide. The agreement of the two methods of counting the  $\alpha$ -particles is in itself a strong evidence of the accuracy obtained in counting the  $\alpha$ -particles expelled per gramme of radium by the electrical method. It is now clear that we have two distinct methods, one electrical and the other optical, for detecting a single  $\alpha$ -particle, and that the employment of either method may be expected to give correct results in counting the number of  $\alpha$ -particles.

Since there is every reason to believe that an  $\alpha$ -particle is an atom of helium, there are now two distinct methods of detecting the expulsion of a single helium atom, one depending on its electrical effect, the other upon the luminosity produced in crystals of zinc sulphide. It is not necessary here to enter upon a discussion of the mechanism of production of a scintillation. In a previous paper, one of us\* has pointed out that there is strong reason to suppose that the molecules of the phosphorescent preparation are dissociated by the  $\alpha$ -particle, and that the luminosity observed may accompany either this dissociation, or the consequent recombination of the dissociated parts.

### *Probability Error.*

We have previously drawn attention to the fact that the number of  $\alpha$ -particles entering a given opening in a given time is conditioned by the laws of probability. E. v. Schweidler† first drew attention to the fact that, according to the theory of probability, the number of  $\alpha$ -particles expelled per second from radio-active matter must be subject to fluctuations within certain limits. If  $z$  is the average number of atoms of active matter breaking up per second, the average error to be expected in the number is  $\sqrt{z}$ . The existence of fluctuations in radiations from active matter of the magnitude to be expected on this theory have been shown by the experiments of Kohlrausch,‡ Meyer and Regener,§ and Hans Geiger.||

In most of the experiments in this paper, an intense source of  $\alpha$ -radiation has been used. If, for example, the source had a  $\gamma$ -ray activity equal to 1 milligramme of radium, the average number of  $\alpha$ -particles expelled per second is  $3.4 \times 10^7$ . The error to be expected is thus 5830 particles, and the relative error  $\sqrt{z}/z$  is  $1/5830$ .

In such a case, we may consider the source as a whole to emit  $\alpha$ -particles at a practically constant rate. The probability variation in the number is beyond the limit of detection by ordinary methods. The case, however, is quite different when we consider the number of  $\alpha$ -particles entering a small opening at a distance from the source. In the experiments, the number entering the detecting vessel varied between two and six per minute, and the number of  $\alpha$ -particles counted in a single experiment varied from 20 to 60. Assuming, for simplicity, that the general theory applies to this case, the probable variation of the observed number from the true mean is equal to

\* Rutherford, 'Phil. Mag.,' July, 1905.

† Schweidler, Congrès International pour l'Étude de la Radiologie, Liège, 1905.

‡ Kohlrausch, 'Wien. Ber.,' p. 673, 1906.

§ Meyer and Regener, 'Ver. d. D. Phys. Ges.,' No. 1, 1908.

|| Geiger, 'Phil. Mag.,' April, 1908.



$\sqrt{z}$ . This amounts to four or five particles for a number 20 and between seven and eight for a number 60. It is not easy to compare accurately theory and experiment in this way, but there is no doubt that the observed variations are of the same order of magnitude as those to be anticipated from the laws of probability.

Some experiments have been made, both by the electric and scintillation methods, to determine the distribution of the  $\alpha$ -particles in time. For this purpose, a thin film of radium was used as a source of rays. A large number of  $\alpha$ -particles was counted, the interval between successive entrances of the  $\alpha$ -particles in the detecting vessel being noted. A curve is then plotted, the ordinates representing the number of  $\alpha$ -particles and the abscissæ the corresponding time intervals between the entrance of successive  $\alpha$ -particles. A curve is obtained like that shown in fig. 4, which is similar in general shape

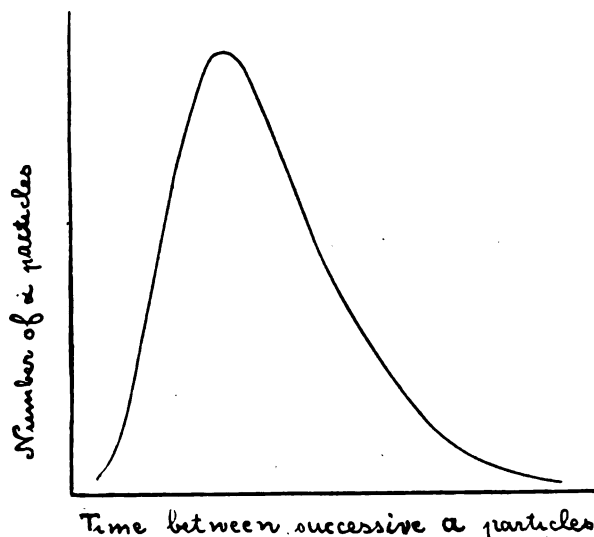


FIG. 4.

to the probability-curve of distribution in time. Further experiments are in progress to determine the distribution-curve as accurately as possible, in order to compare theory with experiment.

#### *Summary of Results.*

(1) By employing the principle of magnification of ionisation by collision, the electrical effect due to a single  $\alpha$ -particle may be increased sufficiently to be readily observed by an ordinary electrometer.

(2) The magnitude of the electrical effect due to an  $\alpha$ -particle depends upon the voltage employed, and can be varied within wide limits.

(3) This electric method can be employed to count the  $\alpha$ -particles expelled from all types of active matter which emit  $\alpha$ -rays.

(4) Using radium C as a source of  $\alpha$ -rays, the total number of  $\alpha$ -particles expelled per second from 1 gramme of radium have been accurately counted. For radium in equilibrium, this number is  $3.4 \times 10^{10}$  for radium itself and for each of its three  $\alpha$ -ray products.

(5) The number of scintillations observed on a properly-prepared screen of zinc sulphide is, within the limit of experimental error, equal to the number of  $\alpha$ -particles falling upon it, as counted by the electric method. It follows from this that each  $\alpha$ -particle produces a scintillation.

(6) The distribution of the  $\alpha$ -particles in time is governed by the laws of probability.

We have previously pointed out that the principle of magnification of ionisation by collision can be used to extend widely our already delicate methods of detection of radio-active matter. Calculation shows that under good conditions it should be possible by this method to detect a single  $\beta$ -particle, and consequently to count directly the number of  $\beta$ -particles expelled from radio-active substances.

Further work is in progress on this and other problems that have arisen out of these investigations.

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*The Charge and Nature of the  $\alpha$ -Particle.*

By Professor E. RUTHERFORD, F.R.S., and HANS GEIGER, Ph.D., John Harling  
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(Read June 18 ; MS. received July 17, 1908.)

In the previous paper, we have determined the number of  $\alpha$ -particles expelled per second per gramme of radium by a direct counting method. Knowing this number, the charge carried by each particle can be determined by measuring the total charge carried by the  $\alpha$ -particles expelled per second from a known quantity of radium. Since radium C was used as a source of radiation in the counting experiments, it was thought desirable to determine directly the charge carried by the  $\alpha$ -particles expelled from this substance. In a paper some years ago,\* one of us has investigated the experimental conditions necessary for an accurate determination of the total charge carried by the  $\alpha$ -rays, and has measured the charge carried by the  $\alpha$ -particles expelled from a thin film of radium itself. In the present experiments the same general method has been used, with certain modifications, rendered necessary by the choice of radium C as a source of  $\alpha$ -rays.

The experimental arrangement is clearly seen in fig. 1. A cylindrical glass tube HH of diameter 4 cm. is closed at the ends by ground-glass stoppers D, E. The source of radiation R is attached to the lower stopper E. The radiation from this passes into the testing chamber, which is rigidly attached to the stopper D by means of an ebonite tube F. The testing chamber consists of two parallel plates A and B about 2 mm. apart. A circular opening, 1.92 cm. in diameter, cut in the brass plate B, is covered by a sheet of thin aluminium foil. The upper chamber AC consists of a shallow brass vessel of aperture 2.5 cm., the lower surface of which is covered also with a sheet of aluminium foil.† The plate B is connected through a side glass tube to one terminal of a battery, the other pole of which is earthed. The chamber AC, which is insulated from the plate B, is connected with one pair of quadrants of a Dolezalek electrometer, the other of which is earthed. The whole apparatus is placed between the poles NS of a large electromagnet marked by the dotted lines in the figure, so that the  $\alpha$ -rays in their passage from the source R to the testing chamber pass through a strong magnetic field.

When the active matter was placed in position, the apparatus was

\* Rutherford, 'Phil. Mag.,' August, 1905.

† The stopping power of each aluminium foil corresponded to about 5 mm. of air.

exhausted by means of a Fleuss pump. The evacuation was then completed by means of a tube of cocoanut charcoal immersed in liquid air. A very low vacuum is required in these experiments in order to reduce the ionisation of the residual gas by the  $\alpha$ -rays to as low a value as possible. If this is not

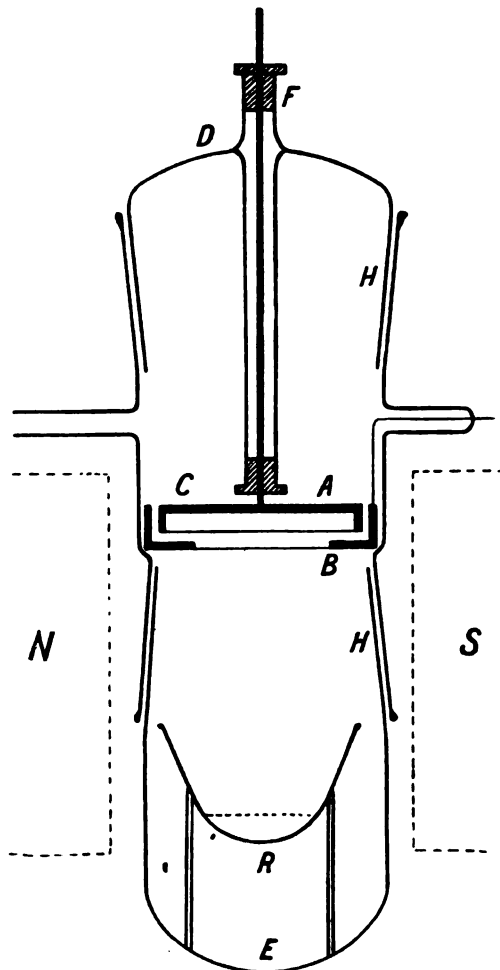


FIG. 1.

done, the positive charge communicated to the upper plate by the absorption of the  $\alpha$ -particles may very rapidly leak away. In addition to the production of a high vacuum, it is necessary to place the testing chamber in a strong magnetic field. It is well known that the  $\alpha$ -particles, in their passage through matter, liberate a large number of slow-velocity electrons, or  $\delta$ -rays, as they have been termed by J. J. Thomson. The presence of a large number

of these negatively-charged particles impinging on the testing chamber completely masks the effect of the positive charge carried by the  $\alpha$ -particles. By placing the testing chamber in a strong magnetic field, these slow-moving particles describe very small orbits, and return to the surface from which they were emitted. In this way the disturbing effect due to the  $\delta$ -rays may be completely eliminated. On account of their very small velocity (about  $10^8$  cm.) and small mass, a magnetic field of only moderate intensity is required for the purpose. It will be observed that the  $\alpha$ -particles are not fired directly into the upper plate AC, but pass first through a thin layer of aluminium foil. This arrangement was adopted in order to diminish as much as possible the number of  $\delta$ -particles set free in the space between the electrodes. The  $\alpha$ -rays pass readily through the thin layer of aluminium at the base of the vessel AC, and are completely stopped by the upper plate. The large number of  $\delta$ -particles emitted from the plate AC by the impact of the  $\alpha$ -rays cannot penetrate back through the aluminium foil, and consequently do not disturb the measurements. It is then only necessary, with the aid of the magnetic field, to get rid of the disturbance due to the  $\delta$ -rays emitted from the two layers of aluminium foil.

In the present experiments the magnetic field served also for another purpose. Radium C emits  $\beta$ - as well as  $\alpha$ -rays, and, in the absence of a magnetic field, these also would be partly absorbed, and give up their negative charges to the upper plate. In the experimental arrangement the magnetic field extended from the source R beyond the testing chamber. The source of radiation was placed about 3.5 cm. below the testing chamber. The strength of the magnetic field was then adjusted, so the  $\beta$ -particles were bent completely away from the lower plate and consequently did not produce any effect in the testing chamber. It was essential for this purpose that the source of radiation was some distance below the plate B, so that the strength of magnetic field obtainable under the experimental conditions and the length of path of the rays were together sufficient to ensure the complete deflection of the  $\beta$ -particles to one side of the glass tube before reaching the plate B.

As the source of radiation was some distance below the testing chamber, it was necessary to use a very active surface of radium C, in order to obtain a reasonably large effect for measurement. For this purpose a small shallow glass cap, represented by the source R in the figure, was attached by a ground-glass joint to a glass tube about 8 cm. long. This was filled with mercury, and the emanation from about 40 milligrammes of radium introduced by the aid of a mercury trough to the top of the cap. The level of the mercury below the top of the cap is represented by the dotted line in the figure. The

emanation was left in the cap for more than three hours, when the amount of radium C deposited on the interior walls of the glass cap and on the surface of the mercury reaches its maximum value. By means of the mercury trough, the emanation was then rapidly displaced, the mercury run out, and the cap removed from the glass tube. The inner surface of the cap was washed first with water and then with alcohol, to remove any trace of grease on the inside of the glass. The inner surface of the cap then acted as a source of intense  $\alpha$ -radiation. Fifteen minutes after removal the  $\alpha$ -radiation is homogeneous, and due entirely to radium C. The active glass cap was then placed in position in the testing vessel, which was then rapidly exhausted by a Fleuss pump. The cocoanut charcoal was then immersed in liquid air and a low vacuum reached in a short time. Usually an interval of 15 to 30 minutes after the removal of the emanation was required for the various operations and to obtain a sufficiently low vacuum for measurements to be started.

In order to determine the amount of radium C deposited in the glass cap, observations of its activity were made by the  $\gamma$ -rays *in situ*. For this purpose a  $\gamma$ -ray electroscope was placed some distance on one side of the apparatus, and the rate of discharge observed at intervals during the experiment. The electroscope was standardised in the usual way by means of the standard preparation of radium placed at the same distance as the source R from the electroscope, so that the amount of radium C distributed on the source at any time was determined in terms of the amount in equilibrium with a definite quantity of radium. Such measurements with the  $\gamma$ -rays can be very simply and accurately made, and, with suitable precautions, the error of observation should not be greater than 1 per cent.

### Method of Calculation.

Using a strong magnetic field, the upper plate received a positive charge, whether the lower plate was charged positively or negatively. The current was first measured with the lower plate charged to a potential  $+V$ , and then with the same plate at a potential  $-V$ . Let  $i_1$  be the current observed in the first case and  $i_2$  in the second case;  $i_2$  is always numerically less than  $i_1$ , the ratio depending upon the degree of exhaustion. Let  $i_0$  be the current through the gas due to the ionisation of the residual gas between the plates by the  $\alpha$ -rays. Then

$$i_1 = i_0 + nE, \quad (1)$$

where  $n$  is the number of  $\alpha$ -particles passing into the upper plate per second and  $E$  the charge on each. On reversing the voltage, the ionisation current is equal in magnitude but reversed in its direction.

Consequently  $i_2 = nE - i_0$ . (2)

Adding (1) and (2),  $nE = \frac{1}{2}(i_1 + i_2)$ .

Let  $Q$  be the quantity of radium C present at any instant measured in terms of the  $\gamma$ -ray effect due to 1 gramme of radium, and  $N$  the number of  $\alpha$ -particles of radium C expelled per second and per gramme of radium. The total number of  $\alpha$ -particles expelled per second from the source  $R$  is  $QN$ . Let  $K$  be the fraction of the total number of  $\alpha$ -particles expelled from the source which impinge on the upper plate. Then  $n = KQN$ , where  $K$  and  $Q$  are measured, and  $N$  is known from the counting experiments. Consequently the charge  $E$  on each  $\alpha$ -particle is given by

$$E = (i_1 + i_2)/2KQN.$$

In preliminary experiments, it was found that the values of  $i_1$  and  $i_2$  were independent of the voltage over the range examined, viz., from 2 to 8 volts. In most of the latter measurements an E.M.F. of  $\pm 2$  volts was used. It was found experimentally that the value of  $\frac{1}{2}(i_1 + i_2)$  was independent of the strength of the magnetic field beyond a certain limit. For example, an increase of the current in the electromagnet from 10 to 20 amperes made no alteration in the magnitude of  $i_1$  or  $i_2$ . A current of 6 amperes gave distinctly smaller values, due to the fact that the strength of the field was not sufficient to bend away all the  $\beta$ -particles completely. In all the final experiments an exciting current of 12 amperes was used. The electromagnet and electrometer connections were well screened and the electrometer readings were remarkably steady. The external  $\gamma$ -ray effect due to the intense source of radiation was screened off as far as possible by plates of thick lead. The apparatus was placed some distance from the electrometer, the insulated connecting wire passing through a long brass tube connected with earth. Notwithstanding these precautions, it was impossible, in consequence of the ionisation due to the  $\gamma$ -rays, to avoid a small back leak of the electrometer system as its potential rose. This was easily corrected for in each observation by observing the rate of movement of the needle over each succeeding 10 divisions of the scale until a deflection of over 150 divisions was reached. The fraction  $K$  of the total number of  $\alpha$ -particles striking the upper plate was determined on the assumption that the  $\alpha$ -particles are emitted equally in all directions. The correctness of this assumption has been verified in other experiments. The distance of the radiant source from the lower plate was determined when in position by a cathetometer. The correction due to the fact that the radiation came from a source of sensible area was determined graphically by dividing up the surface into concentric rings and determining the value of  $K$  for each. In the experiments given

below the mean value of K was 0.0172. The value of N, as determined by the counting experiments, is  $3.4 \times 10^{10}$ . The following tables illustrate the results obtained in two distinct series of experiments:—

Experiment I.

I. No. of observa- tions.	II. Intensity of radiation.	III. Capacity.	IV. $i_1$ .	V. $i_2$ .	VI. $\frac{1}{2}(i_1 + i_2)$ .	VII. E.
1	21.0 mg. Ra	495 cms.	2.24 divs./sec.	1.75 divs./sec.	1.99	$8.8 \times 10^{-10}$
1	18.5 "	495 "	1.74 "	1.55 "	1.68	$8.3 \times 10^{-10}$
2	18.9 "	495 "	1.61 "	1.27 "	1.44	$9.2 \times 10^{-10}$
1	11.4 "	495 "	1.31 "	1.07 "	1.19	$9.6 \times 10^{-10}$
1	10.6 "	495 "	1.19 "	0.92 "	1.05	$9.1 \times 10^{-10}$
2	6.98 "	495 "	0.856 "	0.706 "	0.78	$10.0 \times 10^{-10}$
2	3.08 "	146 "	1.11 "	0.87 "	0.99	$8.7 \times 10^{-10}$
Mean value.....						$9.2 \times 10^{-10}$

Experiment II.

I. No. of observa- tions.	II. Intensity of radiation.	III. Capacity.	IV. $i_1$ .	V. $i_2$ .	VI. $\frac{1}{2}(i_1 + i_2)$ .	VII. E.
2	16.1 mg. Ra	495 cms.	1.90 divs./sec.	1.47 divs./sec.	1.68	$9.3 \times 10^{-10}$
1	14.8 "	495 "	1.63 "	1.28 "	1.45	$9.1 \times 10^{-10}$
2	10.7 "	304 "	2.06 "	1.84 "	1.95	$10.0 \times 10^{-10}$
1	9.8 "	304 "	1.85 "	1.40 "	1.62	$9.9 \times 10^{-10}$
2	6.32 "	146.5 "	2.22 "	1.83 "	2.02	$8.7 \times 10^{-10}$
1	5.16 "	146.5 "	2.02 "	1.46 "	1.72	$9.1 \times 10^{-10}$
Mean value.....						$9.4 \times 10^{-10}$

Column I gives a number of successive sets of observations of the values of  $i_1$  and  $i_2$ ; II, the mean intensity of the  $\gamma$ -ray radiation during the experiment in terms of a milligramme of pure radium; III, the capacity of the electrometer system in cms.; IV and V, the values of  $i_1$  and  $i_2$  expressed in terms of the number of divisions of the scale moved over by the electrometer needle per second; VI, the mean of  $i_1$  and  $i_2$ , also expressed in scale divisions per second; VII, the calculated value of E—the charge on the  $\alpha$ -particle—in electrostatic units. The mean value of E in each complete experiment is obtained by giving a weight to each determination of E equal to number of



observations of  $i_1$  and  $i_2$ . It will be seen that the mean value of  $E$  from experiment I is  $9.2 \times 10^{-10}$ , and from experiment II  $9.4 \times 10^{-10}$ . Taking the mean of these, the value of  $E$  becomes  $9.3 \times 10^{-10}$ . We thus conclude that the positive charge  $E$  carried by an  $\alpha$ -particle from radium C is  $9.3 \times 10^{-10}$  E.S. units.

From other data it is known that the  $\alpha$ -particles from all radio-active products which have been examined are identical. Consequently, we may conclude that each  $\alpha$ -particle, whatever its source, under normal conditions carries the above charge.

*Comparison of the Charge carried by an  $\alpha$ -Particle and a Hydrogen Atom.*

The charge carried by an ion in gases has been determined by a number of observers. Townsend,\* from observations on the electrified gas liberated by the electrolysis of oxygen, concluded that each particle carried a charge of about  $3 \times 10^{-10}$  E.S. unit. Measurements of the charge carried by an ion in gases have been made by J. J. Thomson,† H. A. Wilson,‡ Millikan and Begeman,§ using the now well-known method of causing a deposition of water on each ion by a sudden expansion. The final value of  $e$  obtained by J. J. Thomson was  $3.4 \times 10^{-10}$  unit, by Wilson  $3.1 \times 10^{-10}$ , and by Millikan  $4.06 \times 10^{-10}$ .

From the values found by these experimenters, it will be seen that the value  $E$  of the charge carried by an  $\alpha$ -particle ( $9.3 \times 10^{-10}$  unit) is between  $2e$  and  $3e$ . On the general view that the charge  $e$  carried by an hydrogen atom is the fundamental unit of electricity, we conclude that the charge carried by an  $\alpha$ -particle is an integral multiple of  $e$  and may be either  $2e$  or  $3e$ .

We shall now consider some evidence based on radio-active data, which indicates that the  $\alpha$ -particle carries a charge  $2e$  and that the ordinarily accepted values of  $e$  are somewhat too small.||

*First Method.*—We shall first of all calculate the charge  $E$  carried by an  $\alpha$ -particle on the assumption that the heating effect of radium is a measure of the kinetic energy of the  $\alpha$ -particles expelled from it. There is considerable

\* Townsend, 'Phil. Mag.', February, 1898; March, 1904.

† J. J. Thomson, 'Phil. Mag.', March, 1903.

‡ H. A. Wilson, 'Phil. Mag.', April, 1903.

§ Millikan and Begeman, 'Phys. Rev.', Feb., 1908, p. 197.

|| In a recent paper, Regener ('Verh. d. D. Phys. Ges.', vol. 10, p. 78, 1908) has deduced from indirect data that an  $\alpha$ -particle carries a charge  $2e$ . The number of scintillations from a preparation of polonium were counted and assumed to be equal to the number of  $\alpha$ -particles emitted. A comparison was then made with the number of  $\alpha$ -particles deduced from measurements of the ionisation current, and from the data given by Rutherford of the number of ions produced by an  $\alpha$ -particle.

indirect evidence in support of this assumption, for it is known that the heating effect of the  $\beta$ - and  $\gamma$ -rays together is not more than a few per cent. of that due to the  $\alpha$ -rays. If  $m$  be the mass of an  $\alpha$ -particle and  $u$  its initial velocity of projection, the kinetic energy of the  $\alpha$ -particle

$$= \frac{1}{2}mu^2 = \frac{1}{2} \frac{mu^2}{E} \cdot E.$$

Now, in a previous paper,\* one of us has accurately determined, from the electrostatic deflection of the  $\alpha$ -rays, the values of  $\frac{1}{2} \frac{mu^2}{E} \cdot E$  for each of the four sets of  $\alpha$ -particles expelled from radium in equilibrium, and has shown that the kinetic energy of the  $\alpha$ -particles from 1 gramme of radium in equilibrium is  $4.15 \times 10^4 NE$  ergs,† where  $N$  is the number of radium atoms breaking up per second.

Now the heating effect of the standard preparation of radium was 110 gramme-calories per gramme per hour. This is mechanically equivalent to  $1.28 \times 10^6$  ergs per second. Equating the kinetic energy of the  $\alpha$ -particles to the observed heating effect,

$$4.15 \times 10^4 NE = 1.28 \times 10^6.$$

Substituting the known value  $N = 3.4 \times 10^{10}$ ,

$$E = 9.1 \times 10^{-10} \text{ E.S. unit.}$$

The agreement of the calculated with the observed value is somewhat closer than one would expect, taking into consideration the uncertainty of the data within narrow limits.

*Second Method.*—We shall now calculate the charge  $e$  carried by a hydrogen atom from the known period of transformation of radium. As a result of a series of experiments, Boltwood‡ has shown that the period of transformation of radium can be very simply measured. He concludes that radium is half transformed in 2000 years. Let  $P$  be the number of hydrogen atoms present in 1 gramme of hydrogen. Then the number of atoms of radium present in 1 gramme of radium is  $P/226$ , since, according to the latest determinations, the atomic weight of radium is about 226. If  $\lambda$  is the transformation constant of radium, the number of atoms breaking up per second per gramme of radium is  $\lambda P/226$ . On the probable assumption that each atom breaks up with the expulsion of one  $\alpha$ -particle, this is equal to the number  $N$  of  $\alpha$ -particles expelled per second per gramme. The value of  $N$  from the counting

\* Rutherford, 'Phil. Mag.,' October, 1906.

† The value of  $E$  in the original paper is given in electromagnetic units. For uniformity, it is reduced here to electrostatic units.

‡ Boltwood, 'Amer. Journ. Sci.,' June, 1908.

experiments is  $3.4 \times 10^{10}$ , consequently  $\lambda P/226 = 3.4 \times 10^{10}$ . From data of the electrolysis of water, it is known that

$$\begin{aligned}Pe &= 9.6 \times 10^4 \text{ electromagnetic units,} \\ &= 2.88 \times 10^{14} \text{ E.S. units,}\end{aligned}$$

where  $e$  is the charge carried by the hydrogen atom. Dividing one equation by the other, and substituting the value of  $\lambda = 1.09 \times 10^{-11}$  deduced from Boltwood's measurements, we have  $e = 4.1 \times 10^{-10}$  E.S. unit.

This is a novel method of determining  $e$  from radio-active data. If two  $\alpha$ -particles instead of one are expelled during the breaking up of the radium atom, the value of  $e$  is twice the above value, or  $8.2 \times 10^{-10}$ . This is a value more than twice as great as that determined by other methods, and is inadmissible.

*Discussion of the Accuracy of the Methods of Determination of e.*

We have found, experimentally, that the  $\alpha$ -particle carries a positive charge  $E$  of  $9.3 \times 10^{-10}$  unit. If the  $\alpha$ -particle has a charge equal to  $2e$ , the value of  $e$ , the charge on a hydrogen atom, becomes  $4.65 \times 10^{-10}$ . This is a somewhat higher value than those found in the measurements of J. J. Thomson, H. A. Wilson and Millikan. It is also somewhat greater than the value deduced above from considerations based on the life of radium. As an accurate knowledge of the value of  $e$  is now of fundamental importance, we shall briefly review some considerations which indicate that the values of  $e$  found by the old methods are probably all too small. It is far from our intention to criticise in any way the accuracy of the measurements made by such careful experimenters, but we merely wish to draw attention to a source of error which was always present in their experiments, and which is exceedingly difficult to eliminate. In the experiments referred to, the number of ions present in the gas are deduced by observing the rate of fall of the ions when water has been condensed upon them by an adiabatic expansion. It is assumed that there is no sensible evaporation of the drops during the time of observation of the rate of fall. There is no doubt, however, that evaporation does occur, and that the diameter of the drops steadily decreases. A little consideration of the methods of calculation used in the experiment shows that the existence of this effect gives too large a value for the number of ions present, and, consequently, too small a value of  $e$ . The correction to be applied for this effect is no doubt a variable, depending upon the dimensions of the expansion vessel and other considerations. If the error due to this effect were about 30 per cent. in the experiments of J. J. Thomson and H. A. Wilson, and 15 per cent. in the experiments of Millikan, the corrected

value of  $e$  would agree with the value  $4.65 \times 10^{-10}$  deduced from measurements of the charge carried by an  $\alpha$ -particle.

The determination of  $e = 4.1 \times 10^{-10}$  from the period of transformation of radium is for other reasons probably also too small. The method adopted by Boltwood is very simple, and involves only the comparison of two quantities of radium by the emanation method. Suppose that we take a quantity of an old mineral containing 1 gramme of uranium and determine by the emanation method the quantity  $R$  of radium present. Since the uranium is in equilibrium with ionium—the parent of radium—and radium itself, the rate of production  $q$  of radium by the disintegration of its parent ionium must be equal to the rate of disintegration  $\lambda R$  of radium itself. Now by chemical methods the ionium is separated from the mineral and the rate of growth  $q$  of radium from it determined. Consequently,  $q = \lambda R$ , or  $\lambda = q/R$ . The ratio  $q/R$  can be determined with considerable accuracy by the emanation method and does not involve any consideration of the purity of the radium standard. As Boltwood points out, the accuracy of the method of determination is mainly dependent upon the completeness of the separation of ionium from the mineral. If all the ionium is not separated, the value of  $\lambda$  is too small and the period of transformation consequently too long. For example, if 10 per cent. of the ionium had remained unseparated in the experiments, the period of radium would be 1800 years instead of 2000, and the charge carried by the hydrogen atom calculated from this data would be nearly  $4.6 \times 10^{-10}$  instead of  $4.1 \times 10^{-10}$ .

Considering the data as a whole, we may conclude with some certainty that the  $\alpha$ -particle carries a charge  $2e$ , and that the value of  $e$  is not very different from  $4.65 \times 10^{-10}$  E.S. unit.\*

#### *Atomic Data.*

We have seen that the method of counting the  $\alpha$ -particles and measuring their charge has supplied a new estimate of the charge carried by the  $\alpha$ -particle and the charge carried by a hydrogen atom. The atomic data deduced from this are for convenience collected below:—

Charge carried by a hydrogen atom =  $4.65 \times 10^{-10}$  E.S. unit.

Charge carried by an  $\alpha$ -particle =  $9.3 \times 10^{-10}$  E.S. unit.

Number of atoms in 1 gramme of hydrogen =  $6.2 \times 10^{23}$ .

Mass of the hydrogen atom =  $1.61 \times 10^{-24}$  gramme.

Number of molecules per cubic centimetre of any gas at standard pressure and temperature =  $2.72 \times 10^{19}$ .

\* It is of interest to note that Planck deduced a value of  $e = 4.69 \times 10^{-10}$  E.S. unit from a general optical theory of the natural temperature-radiation.

*Nature of the  $\alpha$ -Particle.*

The value of  $E/M$ —the ratio of the charge on the  $\alpha$ -particle to its mass—has been measured by observing the deflection of the  $\alpha$ -particle in a magnetic and in an electric field, and is equal to  $5.07 \times 10^3$  on the electromagnetic system.\* The corresponding value of  $e/m$  for the hydrogen atom set free in the electrolysis of water is  $9.63 \times 10^3$ . We have already seen that the evidence is strongly in favour of the view that  $E = 2e$ . Consequently  $M = 3.84m$ , i.e., the atomic weight of an  $\alpha$ -particle is 3.84. The atomic weight of the helium atom is 3.96. Taking into account probable experimental errors in the estimates of the value of  $E/M$  for the  $\alpha$ -particle, we may conclude that *an  $\alpha$ -particle is a helium atom, or, to be more precise, the  $\alpha$ -particle, after it has lost its positive charge, is a helium atom.*

Some of the consequences of this conclusion have already been discussed some time ago in some detail by one of us.† It suffices to draw attention here to the immediate deduction from it of the atomic weight of the various products of radium. There is direct evidence in the case of radium that each of the  $\alpha$ -ray changes is accompanied by the expulsion of one  $\alpha$ -particle from each atom. Consequently, since the atomic weight of radium is 226, the atomic weight of the emanation is 222 and of radium A 218. Our information is at present too scanty to decide with certainty whether a mass equal or comparable with that of an  $\alpha$ -particle is expelled in the  $\beta$ -ray or rayless changes.

It is of interest to note that a recent determination by Perkins‡ of the molecular weight of the emanation from a comparison of its rate of diffusion with that of mercury vapour gives a value 235. The earlier estimates of the molecular weight from diffusion data were much lower, but more weight is to be attached to the recent value since mercury, like the emanation, is monatomic, and has an atomic weight comparable with it.

*Calculation of Radio-active Data.*

We are now in a position to calculate the magnitude of some important radio-active quantities.

(1) *The Volume of the Emanation.*—One atom of radium, in breaking up, emits one  $\alpha$ -particle and gives rise to one atom of emanation of atomic mass 222. Since  $3.4 \times 10^{10}$   $\alpha$ -particles are expelled per second per gramme of radium, the number of atoms of emanation produced per second is the

\* Rutherford, 'Phil. Mag.,' October, 1906.

† 'Radio-activity,' 2nd Edition, pp. 479—486; 'Radio-active Transformations, Chapter VIII.

‡ Perkins, 'Amer. Journ. Sci.,' June, 1908.

same. Now we have shown that there are  $2.72 \times 10^{19}$  molecules in 1 c.c. of any gas at standard pressure and temperature. The volume of the emanation produced per second per gramme is consequently  $1.25 \times 10^{-9}$  c.c. The maximum volume is equal to the rate of production divided by the value of the radio-active constant  $\lambda$ , which is equal to  $1/468000$ . The maximum volume of the emanation from 1 gramme of radium is consequently 0.585 cubic mm.

(2) *Rate of Production of Helium.*—Since an  $\alpha$ -particle is an atom of helium, the number of atoms of helium produced per second per gramme of radium in equilibrium is  $4 \times 3.4 \times 10^{10}$ . The factor 4 is introduced, since there are 4  $\alpha$ -ray products in radium in equilibrium, each of which emits the same number of  $\alpha$ -particles per second. Consequently the volume of helium produced per gramme is  $5.0 \times 10^{-9}$  c.c. per second, which is equal to 0.43 cubic mm. per day, or 158 cubic mms. per year. An accurate experimental determination of the rate of production of helium by radium would be of great interest.

(3) *Heating Effect of Radium.*—If the main fraction of the heat emission of radium is a result of the kinetic energy of the expelled  $\alpha$ -particles, its value can at once be calculated. The converse problem has already been discussed earlier in the paper. It will be seen from the numbers there given that the heat emission of radium should be slightly greater than 113 gramme-calories per gramme per hour.

(4) *Life of Radium.*—From the inverse problem discussed earlier, this works out to be 1760 years, supposing the charge on a hydrogen atom equals  $4.65 \times 10^{-10}$ .

For convenience, the calculated values of some of the more important radio-active quantities are given below :—

Charge on an  $\alpha$ -particle =  $9.3 \times 10^{-10}$  E.S. unit.

Number of  $\alpha$ -particles expelled per gramme of radium itself,  
=  $3.4 \times 10^{10}$ .

Number of atoms of radium breaking up per second =  $3.4 \times 10^{10}$ .

Volume of emanation per gramme of radium = 0.585 cubic mm.

Production of helium per gramme of radium per year = 158 cubic mms.

Heating effect per gramme of radium = 113 gramme-calories per hour.

Life of radium = 1760 years.

Calculations of the magnitude of a number of other radio-active quantities can be readily made from the experimental data given in this paper. For lack of space we shall not refer to them here.

*On the Scattering of the  $\alpha$ -Particles by Matter.*

By H. GEIGER, Ph.D., John Harling Fellow, University of Manchester.

(Communicated by Professor E. Rutherford, F.R.S. Read June 18; MS. received July 17, 1908.)

In the course of the experiments undertaken by Professor Rutherford and myself to determine accurately the number of  $\alpha$ -particles expelled from 1 gramme of radium, our attention was directed to a notable scattering of the  $\alpha$ -particles in passing through matter. The effect of scattering is well known in the case of  $\beta$ -particles. A narrow pencil of  $\beta$ -rays emerges after passing through a metal plate as an ill-defined beam. A similar effect, but to a much smaller extent, was known to exist also for the  $\alpha$ -particles. Professor Rutherford\* showed that the image of a narrow slit produced by the  $\alpha$ -rays on a photographic plate broadens out when the slit was covered with a thin sheet of mica, while a well-defined image was obtained in vacuum with the uncovered slit. The question of the actual existence of the scattering effect of the  $\alpha$ -particles has been discussed further by Kucera and Masek,† by W. H. Bragg,‡ L. Meitner,§ and E. Meyer.||

Some experiments have been made, using the scintillation method to determine the magnitude of the scattering of the  $\alpha$ -particles in passing through matter. The apparatus used is shown in fig. 1. The main part consists of

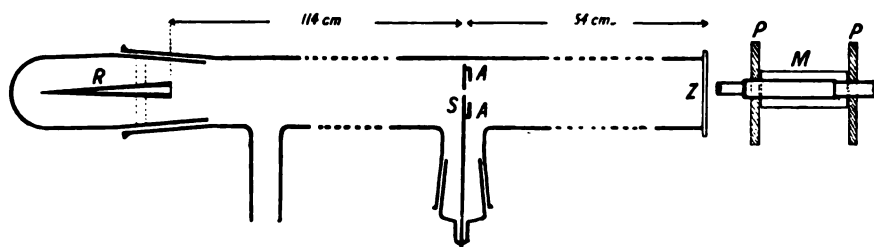


FIG. 1.

a glass tube nearly 2 metres in length and of about 4 cm. diameter. The  $\alpha$ -particles from a strong but small source placed at R passed through a narrow slit S and produced an image of this slit on a phosphorescent

\* E. Rutherford, 'Phil. Mag.,' vol. 12, p. 143, 1906.

† Kucera and Masek, 'Phys. Z. S.,' vol. 7, p. 650, 1906.

‡ W. H. Bragg, 'Phil. Mag.,' vol. 13, p. 507, 1907.

§ L. Meitner, 'Phys. Z. S.,' vol. 8, p. 489, 1907.

|| E. Meyer, 'Phys. Z. S.,' vol. 8, p. 425, 1907.

screen Z, which was cemented to the end of the glass tube. The breadth of the slit was 0.9 mm., and the breadth of the geometrical image on the screen was about 2 mm., depending upon the dimensions and the distance of the source. The numbers of scintillations at different points of the screen were counted directly by means of a suitable microscope M, of 50 times magnification. The area of the screen which could be seen through the microscope was about 1 mm.<sup>2</sup> The number of scintillations counted varied between two or three a minute and about 80 per minute. As regards the microscope and the most convenient method to count the scintillations, the hints given by E. Regener\* in his recent paper proved very useful. The microscope was mounted on a slide PP so that the scintillations produced at varying distances from the centre of the beam could be observed. The actual position of the microscope was read on a millimetre scale fixed to the slide.

The first experiments were made with radium C, which had been deposited on a small piece of metal, as a source of  $\alpha$ -rays; but it soon became obvious that, owing to its comparatively quick rate of decay, it was impossible to get any definite results. To avoid this difficulty, the emanation from several milligrammes RaBr<sub>2</sub> was enclosed under a low pressure in a sloping glass tube R, as seen in the figure. One end of this tube, which was of less than 2 mm. internal diameter, was closed airtight by a thin sheet of mica through which the  $\alpha$ -particles could freely escape. In this way an intense source of small cross-sectional area was obtained, and the scintillations on the screen could easily be counted at different points without any corrections for the decay.

In a good vacuum, hardly any scintillations were observed outside of the geometrical image of the slit. But on allowing a little air into the tube, the area where scintillations were observed greatly increased. By moving the microscope along the whole screen and counting the number of scintillations at definite intervals, usually every second millimetre, a curve of the distribution of the  $\alpha$ -particles was obtained. The number of scintillations was small at the extreme boundary of the screen but rapidly increased towards the centre of the beam.

Similar results were obtained in a vacuum, if the slit were covered with leaves of gold or aluminium. The leaves were attached to small frames and were put into a slide AA connected with the slit S. The distribution of the particles hitting the screen was measured in the same way as before. The figure 2 shows some typical examples of the curves which were obtained. The curve A shows the distribution of the scintillations in a charcoal vacuum. A slight scattering was also observed in this case, which was probably due to

\* E. Regener, 'Verhdlg. d. D. phys. Ges.,' vol. 10, p. 78, 1908.



the last traces of air in the tube. The second curve B shows the effect if the slit is covered with one gold leaf. The area over which the scintillations were observed was much broader and the difference in the distribution could easily be noticed with the naked eye. The actual measurements are given in the curve B. The third curve C shows the effect of two gold leaves together.

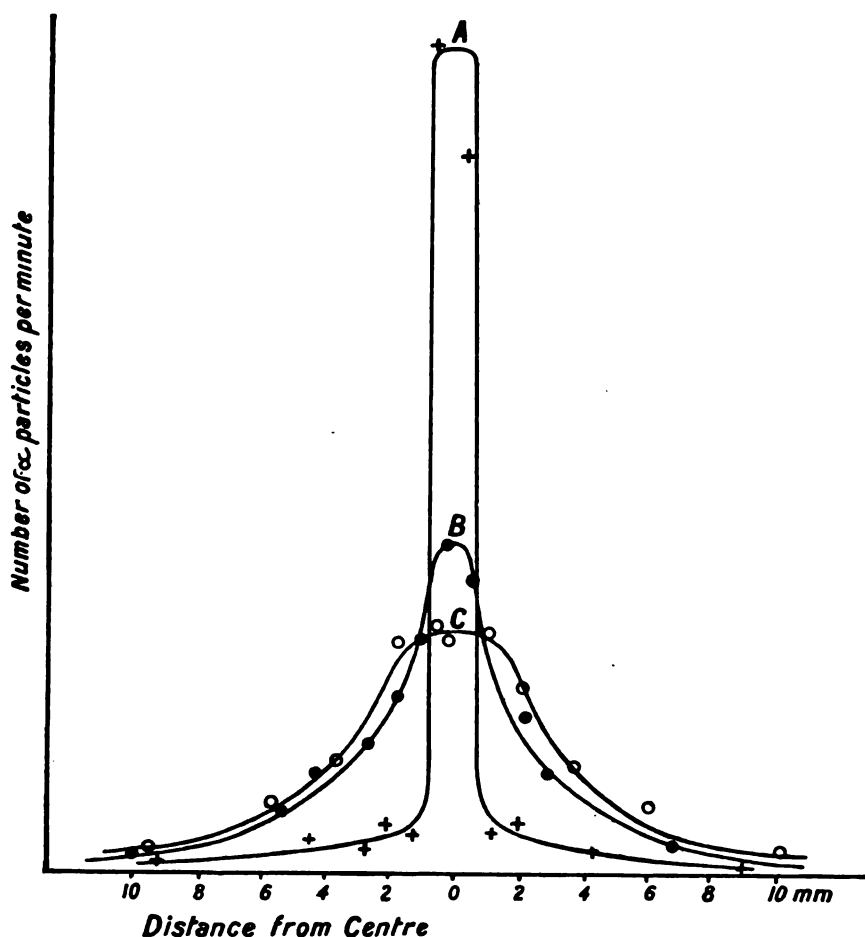


FIG. 2.

The curves as given in fig. 2 are corrected for the absorption in the metal foils. Some absorption took place, since  $\alpha$ -particles of different velocity were present.

Some experiments were also made, using aluminium foil. The aluminium foil showed the scattering effect clearly, but to a much smaller extent than gold leaf, if equivalent thicknesses were used.

The observations just described give direct evidence that there is a very marked scattering of the  $\alpha$ -rays in passing through matter, whether gaseous or solid. It will be noticed that some of the  $\alpha$ -particles after passing through the very thin leaves—the stopping power of one leaf corresponded to about 1 mm. of air—were deflected through quite an appreciable angle. The experiments are being continued with all substances for which it is possible to get thin samples in the hope of establishing some connection between the scattering power and the stopping power of these materials. A fuller investigation will also enable us to treat the matter from a theoretical point of view.

In conclusion, I desire to express my thanks to Professor Rutherford for the kind interest he has taken in these experiments.

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*A Search for Possible New Members of the Inactive Series of Gases.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

(Received June 22,—Read June 25, 1908.)

The gases of the inactive series are five in number, if the emanations from radium, thorium, and actinium be excluded. Beginning with helium, of atomic weight 4, neon follows, with atomic weight 20 ; then argon 40, krypton 82, and xenon 128. It is conceivable that a gas lighter than helium might be found ; an attempt was made by Mr. J. E. Coates, working in my laboratory in 1906, to isolate such a gas, but without success.\* The residues "14" and "15," consisting of helium and neon, have now been exhaustively investigated by Mr. Watson.†

There are gaps in the periodic table for two, or possibly three, gases of the inactive series of atomic weight higher than that of xenon. Owing to the kindness of M. Georges Claude, M. Helbronner, and the directors of the "Société Air Liquide," all the heavier portions of gas remaining after the fractional distillation of no less than 120 tons of air were delivered here from their works at Boulogne, near Paris. The investigation was carried out almost entirely by Professor Moore, to whom the account which follows is due.‡ As will be seen, no positive result has been obtained ; but it is rendered exceedingly unlikely that any stable gas of the inert series with atomic weight higher than that of xenon exists in the atmosphere. It is possible to go further ; it may be stated with certainty that if such heavier gases exist they must be found in the atmosphere. From the known gradation of properties in passing from helium to xenon, it is certain that the missing elements must also be gases ; and it is almost equally certain that they would form no compounds. The methods of separation of these gases, though laborious, are simple ; it is not possible to overlook them, or to fail to recognise them spectroscopically, if present. Hence it follows that, if they are not found in the atmosphere, they either do not exist at all or they are so unstable that they decompose or "disintegrate" during the processes of separation.

Now, three gases are known which do "disintegrate" very rapidly, and which are as inactive as those of the argon group ; these are the emanations

\* See 'Proceedings,' A, vol. 78, p. 479.

† See *infra*, p. 181.

‡ See *infra*, p. 195.

from radium, thorium, and actinium. While the half-life period of the first is 3·8 days, that of the second is 54 seconds, and of the third 4½ seconds. Attempts to determine the molecular weights of the emanations of radium and thorium have been made by P. Curie and Danne; by Rutherford and Miss Brooks; by Bumstead and Wheeler; and by Makower. Curie and Danne\* obtained the number 176; Bumstead and Wheeler,† 180; Makower's first experiment gave 170; and Rutherford and Miss Brooks arrived at a similar number, for the radium emanation. As all the inactive gases are monatomic, it is to be presumed that the emanations resemble them in this respect; hence the molecular weight is identical with the atomic weight. The atomic weight of radium emanation may therefore be accepted as about 175. The molecular weight of thorium emanation has also been attempted by Makower,‡ but without very definite results; all that can be said is that it does not greatly differ from that of the radium emanation.

It will conduce to clearness to reproduce a portion of the periodic table, giving the atomic weights of elements near the argon group:—

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
—	N 14 (17)	P 31 (46)	As 75 (45)	Sb 120 (44)	? 164 (44)	Bi 208	?
—	O 16 (16)	S 32 (47)	Se 79 (49)	Te 128 (41)	? 169 (43)	? 212	?
—	F 19 (16·5)	Cl 35·5 (44·5)	Br 80 (47)	I 127 (44)	? 171 (44)	? 215	?
He	Ne 20 (20)	A 40 (43)	Kr 83 (47)	X 130 (42)	? 172 (44)	? 216 (44)	?
4 (16)	Na 23 (16)	K 39 (46·5)	Rb 85·5 (47·5)	Cs 133 (44)	? 177 (44)	? 221	?
Li	Mg 24·5 (15·5)	Ca 40 (47·5)	Sr 87·5 (50)	Ba 137·5 (44·5)	? 182 (44)	? 226	?
7 (16)		etc.		etc.			
Be							
9 (15·5)							

An inspection of this table will show that it is by no means unlikely that the element in the sixth column of atomic weight 172 is the radium emanation; that thorium emanation belongs to Column VII, with atomic weight 216; and that actinium emanation may follow in the eighth column with atomic weight 260. It is reasonable to suppose that the instability increases with rise of atomic weight; and the close approach of the atomic weight 172 to the results of the attempts to determine it experimentally lends additional probability to the order chosen.

\* 'Comptes Rendus,' vol. 136, p. 1314.

† 'American Journ. of Science,' February, 1904.

‡ 'Phil. Mag.,' January, 1905.

There is, however, another view which should be stated. It is this: it is remarkable that not one single element in Column VI has been detected. The natural conclusion is that owing to some unknown cause the elements in this column are peculiarly unstable. This would lead to the possibility that actinium emanation, the least stable of the three, should be placed in this column. Recent experiments by P. B. Perkins,\* made with the accumulated experience of Messrs. Boltwood and Bumstead, render it not improbable that previous diffusion experiments have underestimated the molecular weight of radium emanation, and that its molecular and atomic weight should somewhat exceed that of mercury. If this be 200, then the radium emanation would fall in Column VII, with atomic weight 216; and the atomic weight of 260 would be ascribed to the emanation from thorium. This, however, raises the interesting question which, however, cannot be discussed here, whether an element like thorium, of atomic weight 232, can yield a "product" of higher atomic weight, 260.

It must however, be pointed out that no experiment of the nature of that detailed in Professor Moore's paper can be regarded as final; it is always open to say that had 1000 tons of air been worked up for rare gases, a stable gas heavier than xenon might have been found. But I think that the balance of probability is in the direction indicated.

\* 'American Journ. of Science,' 1908, p. 461.

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*The Spectrum of the Lighter Constituents of the Air.*

By HERBERT EDMESTON WATSON, B.Sc. (Lond.).

(Communicated by Sir William Ramsay, F.R.S. Received June 23,—Read June 25, 1908.)

In 1900, Professors Liveing and Dewar published a paper on "The Lighter Constituents of Air,"\* and gave a table of wave-lengths for nearly 300 lines. Some of these were shown to be produced by hydrogen, helium, and neon, but the greater number were of unknown origin.

A few years later the spectrum of pure neon was published by Baly,† and it was shown that many of Liveing and Dewar's lines were due to that gas, but at the same time 162 lines remained which, in the opinion of that observer, did not belong to neon.

With the view of throwing some light on the matter, and ascertaining more definitely whether there was a constituent of the air of lower atomic weight than helium, Coates‡ fractionated a large quantity of air, but could find no constituents other than hydrogen, helium, and neon on examining the lightest fractions with a small prism spectroscope.

In order, however, to make quite sure of this point, Sir William Ramsay requested me to photograph the spectrum with the Rowland grating at University College, and the results of this work form the material of the present communication. The main object of the research, namely, definite proof of the existence of a new gas, has been unsuccessful, as was to be expected from the preliminary work, but incidentally it has been shown that the neon spectrum is considerably more complicated than was formerly supposed, and a number of new lines have been measured.

*Experimental.*

The method of fractionation of the gas has already been fully described by Coates,§ but it may be as well briefly to recapitulate it. About 73,000 litres of air were continually circulated through the liquefying apparatus at University College until greatly reduced in volume by the condensation of the least volatile portions. The residue was then condensed in portions of about 80 litres in a glass bulb immersed in liquid air boiling

\* 'Roy. Soc. Proc.,' vol. 67, pp. 467—474, 1900.

† 'Phil. Trans.,' A, vol. 202, pp. 183—242, 1903.

‡ 'Roy. Soc. Proc.,' A, vol. 78, pp. 479—482, 1906.

§ *Loc. cit.*

under reduced pressure. Light fractions were boiled off, and the process repeated several times until the volume was reduced to 4700 c.c. The portion of this gas which was not absorbed by charcoal at  $-190^{\circ}$  C. was separated into several fractions. Fraction 1 was pumped off charcoal at  $-205^{\circ}$  C., and fraction 2 at  $-190^{\circ}$  C. These were the two fractions examined spectroscopically. It is worthy of note that analysis showed neither of them to contain any appreciable quantity of hydrogen, this gas only boiling off at a higher temperature.

The form of vacuum tube used was one in which the capillary portion was viewed end on through a quartz plate cemented on with sealing wax. The electrodes were situated in side tubes, so that the spectrum of the gas surrounding them was not photographed as in the experiments of Liveing and Dewar. They were made of stout aluminium wire, and mounted as described by Baly.\* Baly's methods of filling the tubes and adjusting the pressure in them were also adopted, except with regard to removing the last traces of hydrogen from the electrodes, this gas being present in small quantities in the gas to be examined.

The Rowland grating used has a focal length of 10 feet, and is ruled with 14,438 lines to the inch. When finally adjusted, it was found that the centres of lines of different orders upon the same plate were not in the same horizontal line, and consequently it was easy to distinguish lines of different orders. This displacement was slight, and does not appear to have affected the relation between wave-lengths measured in different orders.

The spectra obtained were remarkably free from ghosts, and, in fact, when first set up, the grating was supposed to be perfect in this respect. I have found, however, that on prolonged exposure all the very intense lines are accompanied by four ghosts, the outer pair being some distance from the true line. They were recognised by the property of symmetry about the principal line, and were in several cases used to determine the true position of the latter. If one ghost were masked by another line, the position of the corresponding ghost was calculated by means of the fact that the distance from the principal line is proportional to the wave-length. It is hoped that by this means all spurious lines have been removed from the table of wave-lengths.

The whole spectrum was photographed in the first order, but lines of wave-length less than 4100 were measured in the second order as well. The plates used were Wratten and Wainwright's "Panchromatic," the sensitiveness of which is practically equal for all portions of the spectrum below 7000. For the red region the "spectrum" plates of the same firm

\* *Loc. cit.*

were used, these being sensitive to at least 7900. I am greatly indebted to Dr. Mees for personally making them for me.

It was found preferable to make exposures during the night, as there was less vibration and the temperature remained more constant. The second condition was very important, since it was found possible to obtain first-class plates only when the temperature variation was less than  $1^{\circ}$ ; but the grating being situated in the basement, the variation during one night seldom exceeded  $3^{\circ}$ , and was usually much less. All the plates were taken between the temperatures  $11^{\circ}$  and  $18^{\circ}$  C.

Exposures of about 16 hours were given, this comparatively long time being necessary to show many faint lines which exist in the spectrum. The very strong lines in the orange region were photographed with tubes which had partially run down, in order to avoid over-exposure. In all cases a weak current from an induction coil without a Leyden jar was used, so as to prolong the life of the tubes as much as possible. After each exposure an iron spectrum was photographed below that of the gas, the slit being screened so that the points of the longer lines in the two spectra just met. As the relative positions of the principal neon lines and standard iron lines had been already determined by Baly, it was considered unnecessary to repeat this work. The wave-lengths of iron lines given by Kayser and Runge\* were, however, used to eliminate errors, according to the method described by Baly,† with the exception that the correction applied to the wave-length of a gas line differed from the value deduced from the correction curve by a small number which was constant for any one plate, and of such a magnitude as to make the corrected wave-lengths agree as nearly as possible with Baly's. This procedure is necessary, because the gas and iron spectra were photographed through different portions of the slit and consequently were apt to suffer a slight relative displacement.

The error in the wave-lengths given is difficult to estimate. All the plates were measured at least twice, and the readings in nearly every case agreed within 0.001 cm., a distance corresponding to 0.05 Ångström unit. Usually the agreement was much better. The wave-lengths, as determined from different plates, agreed in general within 0.04 A.U., but those of the very strong and very weak lines sometimes differed by as much as 0.1 A.U., and in such cases they were remeasured. Any values which differed much from those given by Baly were also carefully revised. In the red part of the spectrum, and the region from 5000 to 4000, a number of plates were taken, and it is hoped that the error in the wave-lengths is not greater than

\* 'Brit. Ass. Reports,' 1891, p. 161.

† 'Spectroscopy,' p. 221.



0.03 A.U. This also applies to lines of shorter wave-length than 4000, as they were measured in two orders. Baly has measured nearly all the lines in the remainder of the spectrum, and his results are probably the more accurate since they were deduced from photographs in the second order. The hydrogen, helium, and mercury lines which were found in the spectrum afforded a means of checking the absolute wave-lengths, and the agreement was found to be good throughout.

*The Constituents of the Gas.*

As before mentioned, two fractions of gas were examined, one pumped off charcoal at a temperature of  $-205^{\circ}\text{C}$ . and the other at  $-190^{\circ}\text{C}$ . After a complete series of photographs of each fraction had been taken the gases were sparked for a considerable time with oxygen, and the latter removed by means of phosphorus. This procedure had no effect on the spectrum beyond removing the hydrogen lines, and moreover the two fractions appear to be identical as regards their constituents, the only difference being in the relative intensities of some of the lines.

The spectrum consisted entirely of bright lines, and no trace of nitrogen or carbon compounds could be detected. Three of the brightest mercury lines were obtained from freshly filled tubes, but were only just visible. The small quantity of hydrogen present in the gas before sparking was a source of considerable difficulty since there appears to be at present no reliable table of the wave-lengths of the secondary hydrogen spectrum. Ames\* has published a list of lines obtained from a vacuum tube of hydrogen, and about half these appeared on my plates. No trace of the weaker lines was to be seen, and hence it appeared unlikely that any other hydrogen lines would be present. There were, however, several faint lines on my plates which appeared only occasionally, and these were all found in a list given by Frost† of lines which appeared in a helium tube after running for some time. The region of the spectrum embraced is only from 4723—4358, but from comparison with Hasselberg's original secondary hydrogen spectrum‡ it is concluded that these lines are due to hydrogen. The number of them is 90, of which only nine are given by Ames. It appears, therefore, that there is a spectrum of hydrogen which is seen only under exceptional circumstances, one of the most favourable of which is the presence of a monatomic gas. A further investigation of this point is in progress. Owing to the limited range of Frost's values it is possible that a

\* 'Phil. Mag.,' vol. 30, p. 33, 1890.

† 'Astrophys. Journ.,' vol. 16, p. 104, 1902.

‡ Watts, 'Index of Spectra,' p. 50.

few hydrogen lines have not been removed from the table of wave-lengths, but their number is not likely to be great because the relative intensities of nearly all the lines given were constant on different plates taken with different tubes.

All the helium lines given by Runge and Paschen,\* except the very weakest, were seen and measured, but the helium spectrum was not nearly as strong as that of the neon. In some cases the former was very faint indeed owing to the selective absorption of the helium by the electrodes, and on one plate no trace of the line 5875·8 was to be seen. The lines at 6678 and 3447, however, were very bright on the same plate, and it must be concluded that these are two neon lines almost coincident with the helium lines. The line at 3447 is, moreover, given by Baly as a strong line, though in his tubes the helium was always allowed to run out before a photograph was taken. There appears to be a similar pair at 4713, though I was unable to obtain a plate on which the neon line alone was present. The wave-lengths of the lines concerned are :—

He ...	...	6678·37	4713·25	3447·73
Ne ...	...	6678·50	4713·51	3447·83

and no reason can be at present assigned to their close proximity.

Argon was present in minute traces, even after the exhaustive fractionation the gas had undergone; it is not surprising, therefore, to find that Baly's gas also contained argon, and several lines given by him are due to this substance. All that have been found are given in the tables, and have not been eliminated as have the lines due to gases previously mentioned.

The question which now arises is: What is the origin of the remaining lines? Their number is 321, of which only 115 are given by Baly, and 132 by Liveing and Dewar, and it might well be supposed that some of them are due to elements as yet unknown. Accordingly their wave-lengths were carefully compared with those of the chief nebular lines as measured by Wright,† and the coronal lines given by Lockyer.‡ There was not the slightest indication of the existence of any of these lines in my spectrum. Marshall Watts, in a list of auroral lines,§ assigns some to neon, but the wave-lengths given are not sufficiently accurate to enable definite conclusions to be drawn. In addition, Dyson's|| list of 1200 lines in the chromosphere

\* 'Astrophys. Journ.,' vol. 3, p. 4, 1896.

† 'Astrophys. Journ.,' vol. 16, p. 53, 1902.

‡ 'Roy. Soc. Proc.,' vol. 66, p. 191, 1900.

§ 'Monthly Weather Review,' vol. 35, p. 408, 1907.

|| 'Phil. Trans.,' A, vol. 206, pp. 403—452, 1906.

of the sun was examined. A certain number of approximate coincidences were observed, and are noted in the table of wave-lengths, but it is highly probable that they are merely accidental, for the lines in question are remarkable neither for their intensity nor their character.

This being so, another explanation was looked for. It will be observed that all the lines not given by Baly are of comparatively low intensity, and occur largely in the ultra-violet, and hence it is quite probable that they are really neon lines which were not previously obtained owing to insufficient exposure. Baly's photographs were all in the second order, which for the particular grating used is not nearly as bright as the first, and, moreover, his vacuum tube had a thin glass end which would naturally obliterate much of the ultra-violet light. To confirm this supposition a different sample of neon and helium containing considerably more helium than the former one was photographed. The lines ascribed to neon were all seen, and were identical in intensity with those formerly obtained, so that it appears very unlikely that any gases other than helium and neon were present in either sample. There is, of course, the possibility that a gas very similar to neon in physical properties exists, but the periodic table renders this unlikely, and it is to be expected that a gas with lower atomic weight than helium would resemble this gas substance rather than neon, with the result that its spectrum would be relatively stronger in the second sample examined. It may consequently be stated fairly conclusively that the spectrum of a new gas has not been photographed, but this is by no means synonymous with saying that such a gas does not exist. There are at least three reasons for this. Firstly, it was remarked by Coates that the fractions of air distilled from charcoal at  $-190^{\circ}$  C. contained hardly any hydrogen, this gas boiling off only at a higher temperature. Consequently, it is possible that another gas might behave similarly, and if this were the case its spectrum would probably be masked by that of the nitrogen in the later fractions. Secondly, as already mentioned, the helium in the gas was absorbed by the electrodes more readily than the neon, and a third gas might be absorbed almost at once before its spectrum could be photographed. Thirdly, it has been observed by Cameron and Ramsay\* that helium is absorbed by glass and silica even in the cold, and it is therefore just possible that a monatomic gas of very low atomic weight might pass through these substances with ease, and if this be so it seems unlikely that a lighter constituent of air will ever be isolated.

It still remains to make a few remarks about the tables of Baly, and Liveing and Dewar. Baly makes no mention of the strong line 6334,

\* 'Chem. Soc. Trans.,' vol. 91, p. 1279, 1907.

although it is assigned to neon by Liveing and Dewar. I have been unable to find the reference for this, but it seems likely that the omission is due to a clerical error. The same author also gives several lines not in my list. Some of these I have identified as argon lines, some as ghosts, and a few as belonging to a different order, but the most careful search has failed to reveal any trace of the rest.

The origin of many of Liveing and Dewar's lines is by no means clear. Since these observers liquefied only about 200 litres of air, less than a three-hundredth part of the amount treated by Coates, it does not seem at all likely that they can have obtained any gas which was unnoticed by the latter. Their gas, however, contained considerable quantities of hydrogen, and though it is stated that the hydrogen lines were not usually visible when photographs were taken, owing to the passage of this gas to the positive pole, yet it may have happened that there was hydrogen round the negative pole as well, but that this yielded a hitherto unrecognised spectrum. If this be not admissible, it must be supposed that the negative pole has some peculiar influence upon the gas in its immediate neighbourhood which complicates the spectrum considerably.

The following tables show the wave-lengths obtained, those of Baly, and Liveing and Dewar being added for the sake of comparison. The intensities are given in the usual way, with 10 as maximum, although this method of representing them is wholly inadequate, and in fact misleading. Many lines of apparently the same intensity differ greatly in reality, and the strongest lines are many hundred times as intense as the weakest. 0 represents a line which can just be measured with a low-power microscope. A few weaker lines could be seen with a small lens, but could not be measured, and are omitted. Anything noticeable about a particular line is placed in the column headed "Remarks."

In conclusion, I should like to tender my warmest thanks to Sir William Ramsay for the great interest he has taken in this work, for personally sparking down and repurifying the gases, and for frequently undertaking the laborious process of remaking and refilling the vacuum tubes. Also to Mr. Baly for advice with regard to the use of the grating, and to Mr. Coates for some help in the earlier part of the work.

*Note added July 28.*—Since going to press, the hydrogen spectrum has been completely photographed. Only one hydrogen line was found in the table of wave-lengths, and this has now been removed.

Wave-length.	Intensity.	Baly.	Intensity.	Living and Dewar.	Remarks.
7245·47	2	—	—	7247	The wave-lengths of these red lines carefully standardised from the helium lines 7065·48, 6678·37, 8705·15, 3613·79, and 3854·67
7174·25	2	—	—	7174	
7059·50	2	—	—	7058 vw	
7032·65	3	—	—	7034	
7024·38	2	—	—		
6929·78	6	—	—	6931	
6759·72	1				
6733·17	2				
6717·22	7	·20	1	6716	
6678·50	9	—	—	6678·4	Not Helium 6678·37
6667·05	3				
6652·20	4	—	—	—	Very weak in first fraction
6640·23	1				
6603·10	3				
6599·18	9	·16	4	6601	
6533·08	6	·10	4	6535	
6506·69	9	·72	6	6508	
6444·88	4	·90	1	6446 vw	
6421·89	2				
6409·93	3	·90	1		
6202·43	10	·40	10	6404	
6401·24	6	·26	1		
6383·14	9	·15	8	6382	
6365·23	2				
6352·08	4	·04	1		
6334·65	9	—	—	6334	L. and D. remark that this is a neon line
6331·11	5	·13	1		
6328·39	6	·38	6		
6313·89	5	·94	1		
6304·97	6	·99	8	6304	
6293·98	5	4·04	1		
6276·23	3				
6273·23	3	·26			
6266·69	6	·66	10	6266	
6258·98	3	9·06	1		
6246·90	4	7·00	1	6244	
				6232	
6225·90	3				
6217·44	6	·50	8	6217	
6214·04	5	·13	2		
6205·94	5	6·01	1		
6203·08	1				
—	—	99·34	1		
6193·23	3				
6189·24	3	·30	1		
6182·28	5	·37	10	6183	
—	—	79·90	1		
6175·09	5b	·15	2	6176 vw	Intensity variable
6173·01	1	·02	1		
—	—	66·81	1		
6163·73	6	·79	10	6163	
—	—	57·12	1		
6156·36	1				
6150·46	3	·49	1		
6143·31	7	·28	10	6144	
6142·63	2	—	—	—	Not a very accurate value, the line being so near the last
6128·63	5	·63	8	6128 vw	
6118·20	4	·22	2		
6096·36	6	·37	10	6097	
6074·51	6	·52	10	6075	

Wave-length.	Intensity.	Baly.	Intensity.	Living and Dewar.	Remarks.
6064 ·70	3	·36	1	—	— } Baly's values for — } these four lines Ar. 6043 ·68 } about 0·3 too Ar. 6082 ·69 } low
6046 ·81	3	·06	1	—	
—	—	43 ·20	1	—	
—	—	32 ·32	2	—	
6030 ·20	5	·20	10	6031	Second order. 3013 ·02
—	—	26 ·03	1	—	
—	—	24 ·40	1	—	3012 ·20
6001 ·15	3	·00	1	6001	Second order. 2992 ·47
5991 ·80	4	·72	2	5991	
5988 ·10	4	·00	4	5987 w	Second order. 2974 ·76
—	—	84 ·94	1	—	
5982 ·71	1	—	—	—	Second order. 2974 ·76
5975 ·76	5	·78	8	5976	
5974 ·80	5	·73	6	—	Second order. 2974 ·76
5966 ·44	1	—	—	—	
5965 ·64	3	·50	4	5964 w	Second order. 2974 ·76
5961 ·85	2	·64	1	—	
—	—	49 ·51	1	—	Second order. 2974 ·76
5945 ·02	6	·91	10	5945 s	
5939 ·49	2	·44	1	—	Second order. 2974 ·76
5934 ·65	2	—	—	—	
5919 ·11	4	·08	1	5919 w	Second order. 2974 ·76
5913 ·81	4	·82	1	5914 w	
5906 ·80	5	·54	2	5906 w	Second order. 2974 ·76
5902 ·65	5	·57	4	—	
5898 ·48	1	—	—	—	Second order. 2974 ·76
5891 ·68	0	—	—	—	
5882 ·06	5	·04	8	5882	Second order. 2974 ·76
5873 ·02	5	·04	1	—	
5872 ·27	4	—	—	—	Second order. 2974 ·76
5868 ·59	3	—	—	—	
5852 ·62	10	·65	20	5852·7 vs	Second order. 2974 ·76
5829 ·08	2	—	—	—	
5820 ·29	5	·29	4	5820 s	Second order. 2974 ·76
5816 ·76	2	—	—	—	
5811 ·62	3	—	—	—	Second order. 2974 ·76
5804 ·62	5	·57	1	5804 s	
5770 ·45	0	—	—	—	Second order. 2974 ·76
5764 ·55	7	·54	8	5763 s	
—	—	64 ·20	1	—	Second order. 2974 ·76
5760 ·74	4	·72	1	—	
5748 ·47	5	·44	4	5747	Second order. 2974 ·76
5719 ·35	5	·42	1	5718	
5689 ·96	5	·96	2	5689	Second order. 2974 ·76
5662 ·72	4	·76	1	5662 w	
5656 ·81	4	·80	4	5656	Second order. 2974 ·76
5656 ·16	2	—	—	—	
5652 ·69	2	·67	1	—	Second order. 2974 ·76
—	—	—	—	—	
5589 ·40	1	—	—	5592	Second order. 2974 ·76
5562 ·90	4	·96	2	5561	
5538 ·73	1	—	—	5532	Second order. 2974 ·76
5533 ·73	1	—	—	5503 vw	
—	—	—	—	—	Second order. 2974 ·76
5494 ·52	1	—	—	—	
5448 ·64	2	—	—	5447 vw	Second order. 2974 ·76
5433 ·78	4	·86	1	5432 w	
5420 ·29	0	—	—	—	Second order. 2974 ·76
5418 ·70	2	—	—	5417 vw	
5412 ·80	2	—	—	—	Second order. 2974 ·76
—	—	—	—	—	
5400 ·70	6	·77	4	5409 vw	Second order. 2974 ·76
—	—	00 ·50	4	5400	
—	—	—	—	—	These lines probably not separable in first order

Wave-length.	Intensity.	Baly.	Intensity.	Living and Dewar.	Remarks.
5383·35	1				
5375·15	3				
5372·47	4	—	—	5372	
5360·16	4	—	—	5360	
5355·37	3	—	—	5355	
5349·86	1				
5343·40	7	·41	1	} 5341	A pair. L. and D.
5341·24	7	·25	4		
5333·44	0				
—	—	32·33	4		
5330·90	8	—	—	5330	
5326·55	4				
5316·92	1				
5314·93	0				
5304·91	3	—	—	5304 w	
5298·33	4	—	—	5298 w	
5280·25	1				
—	—	78·50	1		
5274·24	0				
—	—	71·50	1		
5234·14	4	—	—	5234	
5222·45	5	—	—	5222	
—	—	18·30	1		
5214·44	1				
5210·68	3	—	—	} 5209	
5208·93	4	—	—		
5203·97	5	·12	1		
5193·33	4	—	—	5204	
5191·44	2			5192	
5188·68	5	·79	1	5188	
5158·99	1				
5156·77	0				
5154·54	3				
5152·07	4	—	—	5152	
5150·24	0				
5145·06	5	·15	1	5145	
5122·40	4	—	—	5122	
5120·72	0				
5116·64	6	·72	1	5116	
5113·80	3				
5105·84	1				
5080·52	6	·54	1	5080	
5076·73	0				
5074·85	4	—	—	5074	
5037·87	6	·95	1	5038 s	
5036·12	0				
5031·48	5	—	—	5031	
5023·03	0				
5005·28	2				
4995·02	0				
4957·18	3	—	—	4958 w	
4955·56	0				
4945·05	2				
4939·12	2				
4892·18	2				
4885·05	4	—	—	4884 vw	
4868·35	0	—	—	—	Chromosphere 4068·20, int. 2
4866·60	1				
4865·67	2				
4864·52	0				
4863·22	3				
4852·81	2				

Wave-length.	Intensity.	Baly.	Intensity.	Living and Dewar.	Remarks.
4852.56	0				
4843.01	0				
4837.49	5	.54	1	4838 vw	
4827.52	3				
4823.35	1				
4822.06	3				
4818.94	2	—	—	4819 vw	
4817.80	3				
4811.85	0				
4810.22	3	—	—	4811 vw	
—	—	06.24	1		
4800.29	1				
4790.36	2	—	—	4791 w	
4789.66	0	—	—	—	Chromosphere 4789.70, int. 2
4789.07	4	.07	1	—	
4780.45	1	—	—	—	„ 4780.39, int. 1
4758.84	1				
4752.91	5	.88	1	4754 w	
4749.74	4	—	—	—	„ 4749.58, int. 1
4725.32	1				
4721.72	1				
4717.77	0				
4715.50	5	.49	4	4715	
4714.59	1				
4713.31	6	.51	2	—	My reading probably the mean of Baly's and He 4713.25
4712.22	3	.23	2		
4710.21	4	.21	2	4710	
4709.00	5	.00	4		
4704.55	5	.56	4	4704	
4702.68	1				
4687.79	1	—	—	4687 w	
4680.50	0	—	—	4680 w	
4679.30	0				
4678.37	1				
4671.09	0				
4667.58	0				
4661.27	2	—	—	P 4664	
4656.57	3	—	—	4657 w	
4650.07	1	—	—		
—	—	—	—	4647 w	
4645.59	3	—	—		
—	—	—	—	4640 w	
4636.82	0	—	—	4636 w	
4636.27	0				
4628.50	2	—	—	4628 w	Hardly visible in fraction 1. Ar. 4628.60
4618.04	0				
4614.55	1	—	—	4616 w	
4610.07	1	—	—		
—	—	—	—	4589	
4582.61	2	—	—	4583 w	
4582.18	1				
4575.27	3	—	—	—	Brighter in second fraction
4573.14	1	—	—	—	„ „
4566.04	0				
4540.55	3	.48	1	4540	
4538.49	1				
4537.93	4	.39	1	4538	
4536.40	3				
4534.28	1	—	—	—	First fraction only
4526.04	0	—	—	4526 w	Very faint



Wave-length.	Intensity.	Baly.	Intensity.	Living and Dewar.	Remarks.
—	—	—	—	4523 w	
4517 ·98	0	—	—	4518 w	Very faint.
4515 ·04	0	—	—	—	"
4510 ·96	0	·86	1	—	Ar. 4510 ·90
—	—	—	—	4508 w	
—	—	—	—	4500 w	
4501 ·97	0	—	—	—	
4495 ·23	2	—	—	4488 w	
4493 ·43	0	—	—	—	
4477 ·66	0	—	—	—	Doubtful
4475 ·78	0	—	—	—	
4477 ·01	1	—	—	—	
4465 ·79	0	—	—	—	
4460 ·03	0	—	—	4460 vw	"
—	—	50 ·68	1	4457	
4433 ·80	2	—	—	—	
—	—	31 ·14	1	4431	Ar. 4431 ·16, int. 2
—	—	30 ·23	1	4429	Ar. 4430 ·35, int. 4
—	—	26 ·15	2	—	Ar. 4436 ·16, int. 6
4426 ·57	2	·57	1	—	
4424 ·96	2	·96	2	4424	
4422 ·70	3	·69	2	4422	
—	—	14 ·44	1	4413	L. and D. probably H 4412 ·35
4395 ·79	0	—	—	—	Very faint. L. and D. give 4409, 4396, 4392, 4380, 4370 w, and 4365 vw
4363 ·69	0	—	—	4363 w	
4348 ·37	0	—	—	4347 vw	Very faint. ? Ar. 4348 ·11, int. 8
4345 ·33	0	—	—	—	Ar. 4345 ·27, int. 7
4336 ·46	0	—	—	—	
4335 ·57	0	—	—	—	Very faint. Ar. 4335 ·42, Chromosphere 4335 ·49
4334 ·31	2	—	—	4334 w	
4306 ·48	1	—	—	4306 vw	L. and D. 4322 vw, 4315 vw, and 4290 w
4275 ·78	2	—	—	4276	Chromosphere 4275 ·71
4274 ·88	1	—	—	—	
4270 ·41	0	—	—	4270 w	
4269 ·92	1	—	—	—	
4268 ·18	1	—	—	—	
4259 ·56	1	·53	6	4261 w	Ar. 4259 ·50, int. 9
—	—	—	—	—	L. and D. 4258, 4251, 4241, 4234, 4232, 4220, 4218, and 4206, last being a H line
4200 ·84	0	1 ·03	4	—	Ar. 4200 ·80, int. 10, Chromosphere 4200 ·73
4198 ·35	0	·71	4	4198 vw	Ar. 4198 ·40*, int. 10, Chromosphere 4198 ·73
4191 ·08	0	·44	2	—	Ar. 4191 ·02*, int. 10
—	—	90 ·86	2	—	Ar. 4190 ·85, int. 7
4182 ·10	0	·00	2	—	Ar. 4182 ·03, int. 7
4175 ·40	0	—	—	—	
4174 ·60	0	—	—	—	Chromosphere 4174 ·48
—	—	58 ·68	4	—	Ar. 4158 ·63*, int. 10
4157 ·74	0	—	—	—	L. and D. 4151, 4134
4131 ·06	0	—	—	4131	Chromosphere 4130 ·97
—	—	—	—	—	L. and D. 4128, 12, 4099, 86, 80
4071 ·51	0	—	—	—	One plate only
—	—	—	—	—	L. and D. 4063, 43, 37, 3985, 80, 83, 06

\* Kayser's values are 98 ·162, 91 ·841, 58 ·722, and 67 ·78 respectively.

Wave-length.	Intensity.	Baly.	Intensity.	Living and Dewar.	Remarks.
—	—	3899·21	1	3900	Baly's line a ghost
—	—	86·26	1	—	A ghost
—	—	79·49	1	—	L. and D. 3856, 42, 40, 80, 00, 3777, 66
3754·32	3	·31	2	3754	
3733·54	1	—	—	—	L. and D. 3751, 45, 38, 35, 28
3713·27	0	—	—	3713 s	L. and D. 3710
3701·31	5	·30	6	3701	
3694·38	0	—	—	3694 s	
3685·86	4	·84	4	3686	
3682·37	4	·33	4	3683	L. and D. 3664 s, 55, 51
3633·80	5	·78	6	3634	A pair. L. and D. Other constituent of pair He 3634·39
3609·33	3	·27	2	3609 w	L. and D. 3623
—	—	06·61	1	—	Ar. 3606·69, int. 3
3600·32	6	·24	4	3600	
3593·69	8	·67	10	3593 s	
—	—	88·60	1	—	Ar. 3588·64, int. 2
3587·50	0	87·52	1	3587·5 vs	A pair. L. and D.
—	—	·24	1	—	} These lines possibly obscured by halation from 3593
—	—	86·62	1	—	
—	—	67·73	1	—	
—	—	54·39	1	—	
—	—	—	—	—	Ar. 3554·48, int. 5
—	—	—	—	—	L. and D. 3575, 71, 69, 61, 58, 48, 43
—	—	32·30	1	—	
—	—	29·95	1	—	A ghost
—	—	22·92	1	—	"
3520·61	9	·57	8	3521 vs	
3515·32	5	·30	6	3515	
3510·87	4	·87	2	3510 w	L. and D. also give 3504 w
3501·34	5	·34	6	3500	
3498·19	5	·19	6	3498	
—	—	81·94	1	—	A ghost. L. and D. give 3482, 3481
3472·68	6	·70	8	3473 s	
3466·70	5	·72	6	3467	
3464·46	4	·48	6	3464	
3460·61	5	·67	6	3460	
3454·31	5	·30	6	3454	
3450·88	4	·87	4	3451	
3447·83	5	·83	8	3447·7	Not He 3447·73
—	—	38·66	1	—	A ghost
3424·08	3	·05	2	3424	Much brighter in second fraction
3418·03	5	·05	8	3418 s	L. and D. 3417, 07, 04, 3393, 3388
3378·27	0	—	—	3378 s	Doubtful
3375·74	2	·72	1	—	
3370·02	5	·01	6	3370	L. and D. 3374, 72, 67, 68, 62, 60, 58, 45 s, 44, 35 s, 29, 27, 24 s, 19 s, 15, 13, 11, 10, 3297, 54, 50, 44 s, 33, 30, 25, 18 s, 14, 06, 3199
3167·62	2	—	—	3165	
3153·51	2	—	—	—	
3148·70	2	·76	1	—	
3147·82	1	—	—	? 3142	
3126·33	2	·33	1	—	
—	—	92·84	1	—	
—	—	80·05	1	—	

\* For footnote, see p. 192.

Wave-length.	Intensity.	Baly.	Intensity.	Liveing and Dewar.	Remarks.
3079·31	1				
3079·02	1				
3077·08	2	·08	1		
3063·83	2				
3057·51	3	·50	1		
3030·44	2				
3017·47	3				
3013·09	3				
3012·25	3				
2992·57	3				
2982·81	3				
2981·06	1				
2980·81	1				
2979·94	2				
2975·65	1				
2974·89	3				
2949·32	1b				
2947·44	3				
2932·82	2				
2929·47	1				
2913·28	2				
2911·55	1				
2872·74	1				
2862·28	0				
2835·82	1				
2833·04	0				
2825·75	0				
2825·87	0				
2814·77	1				
2796·06	1				
2794·72	0				
2792·89	1				
2775·09	0				
2766·85	0				
2736·19	1				

*An Investigation of the Heavy Constituents of the Atmosphere.*

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When Ramsay and Travers\* first separated krypton and xenon from liquid air residues, they obtained about 12 c.c. of the former gas and 3 c.c. of the latter. On sparking the xenon with oxygen over caustic potash and removing the excess of oxygen with phosphorus, a density of 64 was obtained, which would make this element, on the assumption that it is a monatomic gas, have an atomic weight of 128. This would place it in its proper place in the periodic table—above iodine. Consequently, if any other element of greater density were present in the xenon, the quantity would necessarily be very small.

Afterwards Ramsay† obtained 0.87 c.c. of xenon from 191.1 kilogrammes of air, which plainly indicated that any attempt to look for elements in the atmosphere of greater density than xenon would involve the handling of very large quantities of liquid air.

This difficulty has been surmounted through the courtesy of M. Georges Claude, and M. André Helbronner, of Paris, who very kindly furnished the necessary material. The liquid air apparatus used by them is shown in fig. 1.

The cooled air, under a pressure of about 5 atmospheres, enters H, and ascending the series of tubes F, which are surrounded by liquid oxygen, is liquefied there progressively, that is to say, the oxygen being converted into a liquid at a higher temperature than the nitrogen, liquefies first and drips back into the receiver A. This liquid contains about 48 per cent. of oxygen. The nitrogen meanwhile reaches B, and descending the tube F', is liquefied and collects in C, as almost pure liquid nitrogen. The liquid in A ascends the tube R, and enters the fractionating tower, where the oxygen passes down and ultimately reaches the reservoir M. The nitrogen, carrying traces of oxygen, meanwhile ascends and meets with the nitrogen from C, which has arrived at the top of the tower by means of the tube R'. The last traces of oxygen are thus fractionated from the nitrogen, and the latter gas escapes through E practically pure. This nitrogen and also the oxygen from M, which is used for commercial purposes, is led through "exchangers" (not

\* 'Trans. Roy. Soc.,' Series A, 197.

† 'Roy. Soc. Proc.,' vol. 71, p. 421, 1903.

shown) which are used to lower the temperature of the air, which enters at H. These exchangers completely surround the apparatus shown in fig. 1,

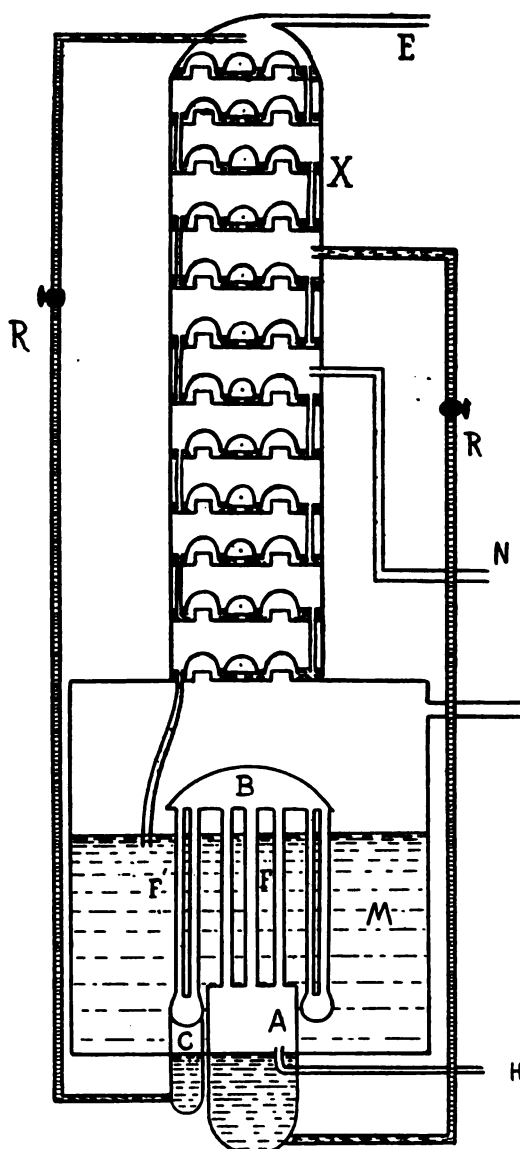


FIG. 1.

and serve to prevent loss of heat energy. This loss, although small, is appreciable, and in order to replace it small quantities of liquid air may be run into the fractionating tower through the pipe N. The efficiency of the whole plant is about 95 per cent.

It can be seen at once that the light gases, helium and neon, would escape through E with the nitrogen, whilst the heavy gases, krypton and xenon, would be concentrated with practically no loss whatever, in the oxygen contained in the reservoir M. The majority of the argon accompanies the nitrogen; a little is retained by the oxygen. Therefore, at the end of any period of operation the oxygen in the reservoir M would contain all of the krypton and xenon, in addition to any other heavier gases which were originally in the air, passed through the apparatus. In this way the krypton and xenon in several tons of air can be concentrated in 10 or 15 litres of liquid oxygen.

The first consignment of oxygen received represented the residues from 3 tons of air. It was contained in a 5-litre vacuum flask, and was allowed to evaporate into the air until only about 1 litre of liquid remained. The flask was then connected with a large gas-holder in which the oxygen was collected as it evaporated. It was expected that the 5 litres of gas which remained behind in the Dewar flask would be very rich in the heavy rare gases, as it constituted the last fraction from 3 tons of air. A preliminary test with a small portion of this gas showed that it was explosive, due to the presence of vapour of pentane which was used for lubricating the compressors at the liquid air plant. The presence of this hydrocarbon was unfortunate, as the 5 litres of gas in the vacuum flask did not contain as much rare gas as it would otherwise have done. The same trouble was met with in all the air that was subsequently worked up. The pentane was got rid of by passing the gas over heated copper oxide, first passing it, however, through a capillary tube sealed on to another tube 5 mm. in diameter, completely filled with a roll of fine copper gauze. When the gas reached the heated copper oxide it exploded back, but only as far as the copper gauze. The flow of gas was regulated so that the explosions took place regularly, but not violently.

In this manner most of the oxygen present was used up in oxidising the pentane. The gas obtained from this treatment was passed over heated copper and a strongly heated mixture of magnesium and lime, in order to remove the last traces of oxygen and nitrogen. It was then stored over mercury.

Meanwhile, another consignment of liquid oxygen had been received from Paris. It represented the residues from 16 tons of air. The oxygen had been allowed to evaporate until it just filled a 5-litre vacuum flask. The process of evaporation was continued at University College until 2 litres only of liquid remained, the gas from this last portion being collected in the same large gas-holder as before. About 2500 litres of gas were thus stored

over water. The last fraction in the vacuum flask was worked up in exactly the same manner as described above, and the resulting rare gas was added to that already obtained.

The gas in the large reservoir consisted principally of oxygen, and in order to obtain the rare gases present this oxygen had first of all to be removed. Using copper to absorb large quantities of oxygen is an extremely slow and laborious process. If a small apparatus is used the copper is very soon oxidised and must be reduced. Each time this change in procedure is made the gas in the apparatus must be pumped out and stored. Large tubes containing a considerable amount of copper are almost equally objectionable. It was therefore determined to make use of melted phosphorus as an absorbing agent instead of copper. The apparatus used is shown in fig. 2.

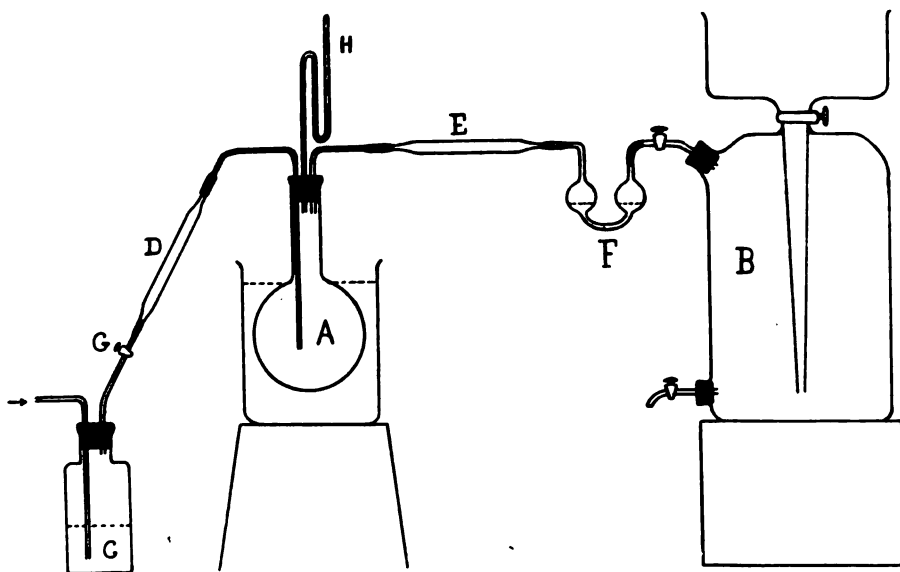


FIG. 2.

C is a wash-bottle containing concentrated sulphuric acid, which served the double purpose of drying the gas and of indicating its rate of flow, which is regulated by the stop-cock G. D and E are phosphorus pentoxide tubes, and F is a bubbler, preferably containing concentrated sulphuric acid. A is a round-bottomed Jena flask of 1 litre capacity, the delivery tube reaching to almost 2 inches above the surface of the melted phosphorus. It is provided with a pressure gauge H. The whole apparatus must be, of course, perfectly air-tight. Connections are made by good pressure tubing fastened with copper wire. At first the apparatus was disconnected from the

receiving reservoir B and completely filled with carbon dioxide. The stopper of H was then quickly removed and half-a-pound of dried phosphorus sticks dropped in. The stopper was then reinserted, wired down, and connection made with the reservoir B, which was filled with dilute sodium hydroxide solution. The temperature of the water bath was then raised to about  $55^{\circ}$  C., and maintained at that point with only slight variations. The oxygen from the large reservoir was then led slowly through the apparatus. Its advent was at once signalled by a bright glow in the flask, which was maintained as long as the gas passed. After once regulating, the apparatus needed very little attention, practically running alone. For the sake of safety, the work was carried on out of doors, but at no time was there an accident or trouble of any kind.

When one charge of phosphorus was used up, the gas in the apparatus was displaced by carbon dioxide, after which another flask with a fresh charge of phosphorus was substituted for the old one. This apparatus was run practically continuously in the day-time for six weeks, during which time 5 pounds of phosphorus were used.

If the gas is rich in oxygen, phosphorus pentoxide is the chief product, some red phosphorus being also found. In the case of a gas poor in oxygen, a good deal of trioxide is produced which distills over and tends to stop up the exit tubes.

About 100 litres of gas remained unabsorbed by the phosphorus. This gas was passed over soda-lime, metallic copper, magnesium-lime mixture, and copper oxide. This last substance oxidised any hydrogen or carbon monoxide given off by the magnesium and lime. Sixteen combustion tubes containing magnesium and lime were required to remove the nitrogen present. The residues in these tubes were kept for further examination. By this means 6 litres of inactive gas were obtained and stored over water.

During the storage of the gas and during the progress of the work itself, nearly 3000 litres of water had been in contact with the gas. Practically all of this water was kept. Although the solubilities of krypton and xenon are not at present known, it is probable that the solubilities of the inactive gases increase with the densities and that the solubility of xenon is something like three times that of argon. That being true, any new gas which might be present of a still higher density would be more soluble than xenon. Although the partial pressure of such a gas in the large gas-holder would be very small, it was deemed advisable to boil at least a portion of the water used in this gas-holder, and all of that used in the smaller ones. This was accomplished by means of an apparatus designed by Lord Rayleigh.\* About

\* 'Phil. Trans.,' A, vol. 186, p. 225, 1895.

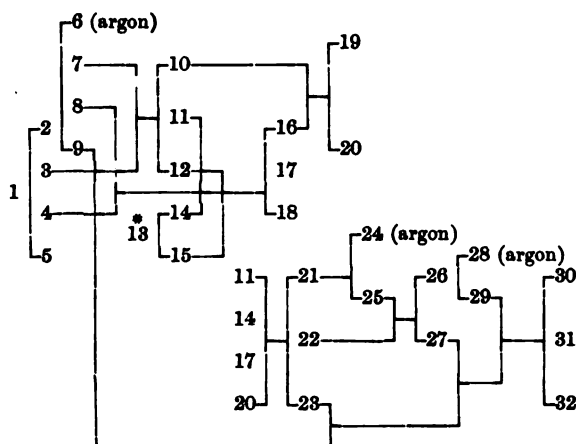


1000 litres of water were boiled in this manner and the evolved gas carefully collected. This gas was passed over copper, magnesium lime mixture, and copper oxide, and the residue added to the stock of inactive gas already obtained. Any further quantities of water with which the gas came into contact during this process were also boiled and the gas worked up in the same manner. Nearly 1 litre of inactive gas was thus obtained from the whole amount of water boiled.

The mixture of the rare gases from the two vacuum flasks was fractionated first. This had been stored over mercury and was run into a bulb immersed in liquid air. The gas readily liquefied. It was then allowed to boil back into the mercury reservoir until a solid began to appear in the fractionating bulb. The liquid air in which the bulb was immersed was removed, and as the solid changed to gas the latter was taken through a Töpler pump and run into another mercury reservoir (fraction 13 below). The volume thus obtained was 200 c.c. The argon, with traces of krypton and xenon, was added to the main body of gas.

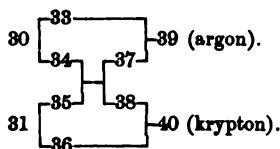
The latter, which consisted mostly of argon, was then fractionated. The same apparatus was used. The gas was run over soda lime and phosphorus pentoxide, and liquefied readily under the water pressure which could be exerted on the gasometer. The ease with which the gas liquefied was due to the large percentage of krypton and xenon present. It was then allowed to evaporate back under reduced pressure into a mercury reservoir and when this was full the gas was readily transferred to the water reservoir. This was continued for two hours, at the end of which time about 1 c.c. of liquid was left in the fractionating tube. This then began to solidify. The surrounding liquid air was removed, and the gas taken through the pump, where it was collected in three fractions, the last one of 15 c.c. (fraction 5 below) showing the xenon spectrum but no krypton lines. The argon (fraction 2 below) was refractionated in the same way once more, and a further supply of heavy gas obtained. The argon this time was allowed to evaporate back into a different gas-holder (fraction 6) containing fresh water, so that the water which had stood in contact with the gas in the other gas-holder could be boiled. The gas obtained from this boiled water was fractionated separately and yielded 3 c.c. of xenon and 9 c.c. of krypton.

The general plan of fractionation followed is illustrated by the following scheme :—



\* Krypton and xenon obtained from vacuum flasks.

11, 14, 17, and 20, which constituted the middle fractions and were mixtures of krypton and xenon, were refractionated together. 30 consisted of krypton containing some argon, 31 was krypton, and 32 xenon. 30 and 31 were still further fractionated in the following manner:—



The total amount of krypton thus obtained was 293 c.c.

Fractions 5, 12, 15, 18, and 32 were all fairly pure xenon and were mixed together. The total volume was 70 c.c. Since xenon boils at  $164^{\circ}$  abs., in order to fractionate it a temperature was required at which xenon had a moderate vapour-pressure. This could be obtained by ethylene boiling under reduced pressure, but as the amount of ethylene required to fractionate 70 c.c. of xenon would be considerable, an easier method of fractionation was looked for. When liquid air is added to petroleum ether, the temperature of the latter gradually falls until a point is reached at which, on adding more air, the petroleum ether at the surface freezes to a white solid. If this is stirred down into the liquid below, a temperature of  $143^{\circ}$  abs. may ultimately be reached. By adding more liquid air every few minutes the temperature may be kept constant within two or three degrees. At  $143^{\circ}$  abs. the liquid is thick and "mushy," and difficult to stir, but at  $153^{\circ}$  abs. it is not nearly so thick and may easily be stirred.

The xenon was run from the mercury gas-holder into a small fractionating bulb connected with a Töpler pump. All the connections were of glass

sealed on. The bulb was immersed in petroleum ether and a temperature of  $148^{\circ}$  to  $151^{\circ}$  abs. was maintained during the fractionation. At a higher temperature than  $151^{\circ}$  abs. the xenon comes off too rapidly. The method employed for fractionation was as follows:—

Xenon.	41	46
	42	47
	43	48
	44	49
	45	50

The five fractions (41 to 45) first obtained were stored in test-tubes over mercury. 41 was run into the fractionating bulb and about two-thirds of the gas pumped off, constituting 46. 42 was then run into the bulb, where one-third of 41 still remained. Two-thirds of the whole volume was pumped off to form fraction 47. 43, 44, and 45 were added in the same manner. An examination of the spectrum of 46 showed that it contained traces of nitrogen and krypton. It was therefore fractionated separately at the temperature of liquid air to remove these impurities. The fractionation of the xenon was carried still further at a slightly lower temperature, viz., between  $143^{\circ}$  and  $145^{\circ}$  abs.:—

46	51		
	52		
	53	54	59
	47	55	60
	48	56	61
	49	57	62
	50	58	63
		64	69
		65	70
		66	71
		67	72

No. 58, which had a volume of about 18 c.c., was fractionated at the same temperature as before. Three or four cubic centimetres were obtained by the first 10 minutes' pumping, and constituted fraction 63; the rate then decreased considerably, two or three bubbles coming off with each stroke of the pump when there was an interval of half a minute between the strokes. This gas was collected in two fractions—64 and 65. When the gas was

obtained at the rate of only one bubble for each stroke, the ether bath was removed and the last fraction pumped off (No. 66).

The final fractionation, giving fractions 67 and 72, was carried out under the same conditions.

No. 72, whose volume was about half of 1 c.c., was sparked with oxygen over caustic potash solution, and the excess of oxygen removed with phosphorus. The photograph of the spark spectrum of this gas was compared on the same plate with that obtained from fraction 59, which was entirely free from krypton. There was no difference whatever in the spectra. No lines occurred in one spectrum which were absent in the other, and the relative intensities of the lines were about the same in the spectra. In other words, no difference was discernible.

The density of fraction 66 was taken in a 7-c.c. bulb, and found to be 63. A density determination was attempted with fraction 72, but the volume was too small to allow of an accurate determination being made.

These negative results were disappointing, but because no new element could be found in 19 tons of air, it did not prove that a positive result could not be obtained with 100 tons. In addition, the large quantities of water with which the gas was in contact at different times—although most of this water was boiled—might after all have been a source of considerable loss. Especially would this be the case if the solubility of the possible new gas were anything like that of the radium emanation, whose solubility coefficient at 18° is 0.270.\* The residues from 100 tons of air were kindly furnished by M. Claude, but in order to eliminate any loss from water, an entirely new plan of procedure was decided upon.

Six 5-litre vacuum flasks were filled with the liquid oxygen. Five of these were fitted with rubber corks through which ran glass delivery tubes with a double bend, the other end of each of these tubes dipping below the surface of the liquid oxygen in the sixth vessel, which was kept full during the progress of the experiment. The arrangement is shown in fig. 3. As the oxygen in the vessels A to E evaporates, the krypton and xenon were condensed to a solid either in the tubes that dropped below the oxygen in F, or in the liquid oxygen itself. The gas left behind in the first five vessels, after evaporation was complete, was of course rich in krypton and xenon. This gas was displaced by a strong solution of caustic soda, and run into wine bottles, which were securely corked, about 10 c.c. of the soda solution being left in each bottle. When the bottle was inverted, this liquid formed an excellent seal. Unfortunately, one of the vacuum flasks was broken, and 5 litres of gas were lost. The glass delivery tubes, which contained a heavy

\* 'Phys. Zeit.,' vol. 9, pp. 6—8, 1907.

white deposit, extending several inches above the surface of the liquid oxygen in F, were cut between F and the other vessels, and the open ends quickly closed by means of rubber tubing and Hofmann screw clamps. They were allowed to remain dipping in the liquid oxygen. This part of the work was kindly carried on at Paris by Mr. W. L. Alton. The bottles of gas, the caustic soda solution, and the vessel full of liquid oxygen and containing the five delivery tubes were sent from Paris to University College.

The five delivery tubes containing solid krypton, xenon, carbon dioxide, etc., were quickly dropped into a flask which was filled with carbon dioxide. This flask was connected with a gas-holder containing caustic soda solution, so that as the solids on the tubes evaporated the soda solution was displaced in the gas-holder. All of the gas in the flask was finally transferred by running into it sodium hydroxide solution.

Meanwhile, the vessel F had been fitted with a rubber stopper and a wide delivery tube leading to the bottom of a vacuum tube containing about 300 c.c. of liquid air. This air was constantly replenished as it evaporated. The object was, as before, to concentrate the rare gases in a smaller volume of liquid air or oxygen. The Dewar tube used was an exceptionally good one, and by filling up late at night and early in the morning the liquid air was never allowed to get too low. At the end of a week, when the oxygen in the vessel F had evaporated, the vacuum tube was connected with a coiled glass condenser dipping in liquid oxygen as indicated in fig. 4.

In order to prevent the liquefaction of the oxygen from the vessel G in the tube H, the exit tube was connected with the pump and the pressure inside the apparatus kept a little below normal. Under these conditions, only krypton and xenon with traces of carbon dioxide and pentane were condensed in the tube H, oxygen with traces of nitrogen escaping through the pump. As krypton has a vapour-pressure at the temperature of liquid oxygen of 17.4 mm., it seemed certain that the procedure adopted would result in the loss of most of the krypton, but as the vapour-pressure of xenon is only 0.17 mm. at the same temperature, it seemed equally certain that a large part of the xenon would be obtained. On the other hand, if the boiling points of the argon series be plotted against their atomic weights, it can be readily shown from the curve obtained that the boiling point of a member of the series with an atomic weight of about 175 would be approximately 183° abs., 20° higher than the boiling point of xenon. Now Ramsay has shown\* that whereas xenon has a vapour-pressure of 0.17 at 90° abs., at 68° abs. a difference of 22° 6, its vapour-pressure is only 0.0005 mm. Therefore, a new element, the boiling point of which differed from that of xenon

\* 'Roy. Soc. Proc.,' vol. 71, p. 421, 1903.

to about the same extent, would have at the same temperature of liquid oxygen, a vapour-pressure so small that practically all of the gas would be obtained by the method of fractionation used. As the object was not to prepare krypton, but to look for new elements in the atmosphere, the work was continued along the same lines.

The solidified gases in the condenser H were allowed to evaporate into the reservoir in which was stored the gas obtained from the five delivery tubes, the last traces of gas being swept out with carbon dioxide. The combined gases in the reservoir were then worked up in the usual manner by passing them over soda-lime, metallic copper, magnesium-lime mixture, and copper oxide. The resulting gas was stored over mercury. On running it into a bulb immersed in liquid air, it solidified at once, but was not fractionated separately, being transferred back to the mercury reservoir through the pump. Its volume was about 50 c.c.

The gas remaining in the large flask F (fig. 3), and in the small tube G (fig. 4), together with that in the wine bottles which contained the gas

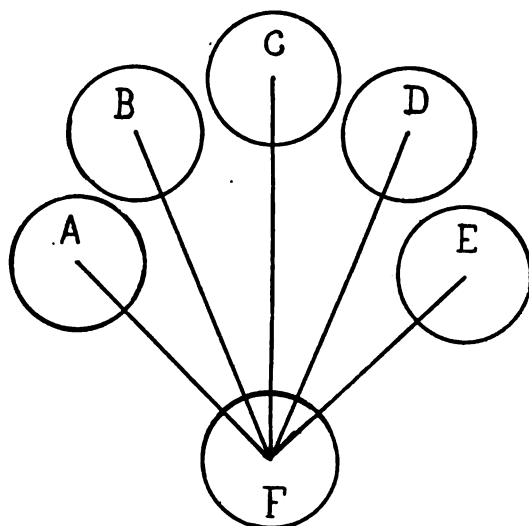


FIG. 3.

transferred from four of the other flasks shown in fig. 3, was purified in the usual manner with magnesium-lime mixture, etc. The inactive gas was mixed with the 50 c.c. already obtained and stored over mercury.

The total volume of water and caustic soda solution which had been in contact with the gas at any period was not more than 20 litres. All of this was carefully kept and thoroughly boiled, the evolved gases being worked up in

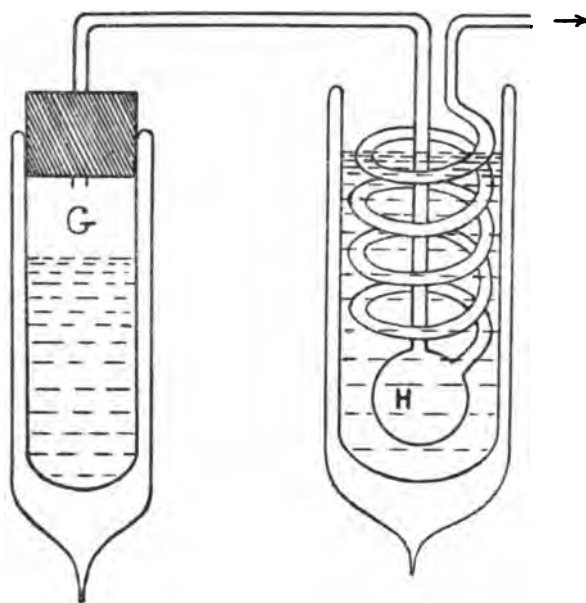
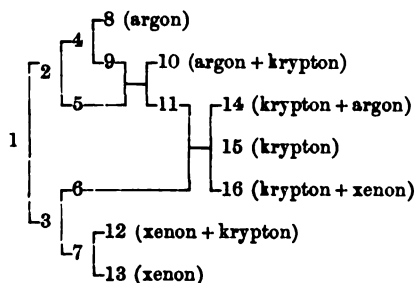


FIG. 4.

the usual manner, and the rare gas obtained added to the main supply. The latter was fractionated in the following manner:—



The main body of the gas constituted fractions 13 and 15, fractions 10, 14, 16, and 12 occupying only a few cubic centimetres each. The volume of the krypton was 50 c.c., and that of the xenon 220 c.c. The second method of extracting the heavy rare gases is therefore nearly as economical, as far as xenon is concerned, as the first, but from five times the amount of air only one-sixth the volume of krypton was obtained. The second method, however, involves very much less labour, and was the better of the two considering the object of the work. Ramsay has shown\* that the proportion of krypton in the air, by volume, is 1 part in 20 millions, and that of xenon 1 part in

\* 'Roy. Soc. Proc.' vol. 71, p. 422, 1903; 'Roy. Soc. Proc.' vol. 80, p. 599, 1908.

170 millions. According to these figures, 100 tons of air ought to yield 4 litres of krypton and 470 c.c. of xenon. The difference between these volumes and those obtained is very marked in the case of krypton. This is not surprising, considering what the vapour-pressure of krypton is at the temperature of liquid air.

By the first method of separation 70 c.c. of xenon was obtained from 19 tons of air, by the second method 220 c.c. from 100 tons, but in the latter case the gas in one of the vacuum flasks was lost. Consequently, the difference in the volume of xenon per ton of air obtained by the two methods is not large. There is, however, loss in both cases, and as the amount of this loss is unknown, the data are insufficient to base a calculation on.

The xenon, after being sparked with oxygen, was fractionated in the same manner as before, the temperature of the petroleum ether being maintained between  $149^{\circ}$  and  $151^{\circ}$  abs. The final  $\frac{1}{3}$  c.c. of gas which could be pumped off whilst the fractionating bulb was still at the above temperature was collected separately. On removing the vacuum tube and allowing the temperature of the bulb to rise, another small fraction of  $\frac{1}{3}$  c.c. was obtained. At the time it was thought that this behaviour was indicative of the presence of a new gas, but in reality it was probably due to the fact that the amount of gas was so small that the evaporation was insufficient to give as much as one bubble for each stroke of the pump. The bulb, therefore, appeared to have been pumped "dry," although a small trace of gas remained. Both the ordinary and spark spectra of these two last fractions were photographed and compared on the same plate with the spectra given by the first fraction at the opposite end of the series. The lines obtained from the three samples of gas were identical. They were compared by using the negative as a lantern slide and throwing the images of the spectra on a screen. In this way the lines could very readily be compared.

The results obtained indicate that if a stable element heavier than xenon does exist in the atmosphere, the volume present compared to that of xenon is extremely small. As at least 10 per cent. of a new gas could probably have been detected in the spectra examined, therefore, 0.03 c.c. of such a gas could have been detected. As this existed in 100 tons of air, it represents 1 part in 2,560,000,000 by volume.

All of the magnesium and lime used to extract nitrogen had been kept in stoppered bottles. Ramsay and Travers tested the magnesium and lime used by them in the preparation of argon, but no tests had been made with such a mixture over which a gas containing a considerable proportion of krypton and xenon had been passed. It was thought possible that although argon and the lower members of the series did not react, those of higher



atomic weight might do so. The magnesium and lime over which the gas containing most krypton and xenon had been passed was therefore treated in the following manner :—

It was placed in the round-bottomed Jena flask A (fig. 5) which was connected with a large U-tube containing pure dilute hydrochloric acid. E is a phosphorus pentoxide tube, one end of which was connected with a Töpler

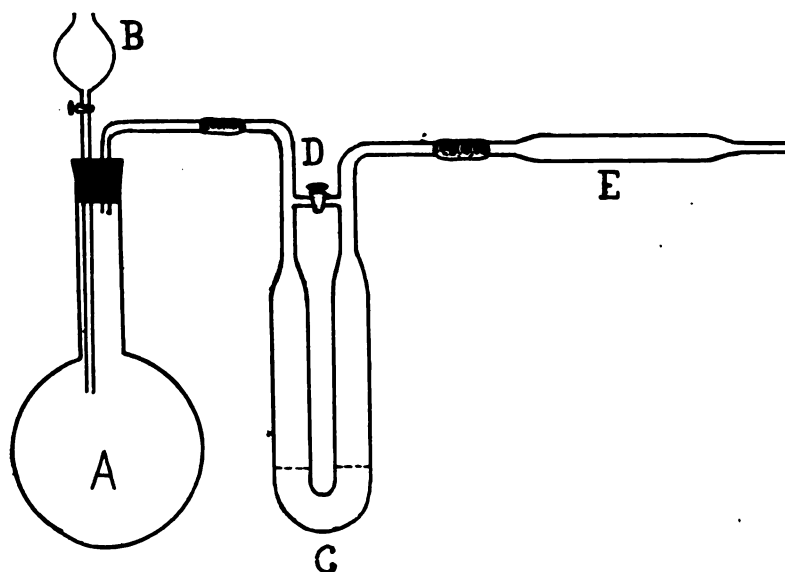


FIG. 5.

pump. The whole apparatus, after being made perfectly air-tight, was exhausted. Connection could be made between the two sides of the U-tube by opening the tap D. When exhausted, the tap D was closed, and water allowed to run in slowly through B. The evolved gas was passed through the acid in C by which the ammonia was retained and the unabsorbed gas was collected at the pump, sparked with oxygen over sodium hydroxide solution and the excess of oxygen removed by means of phosphorus. The two or three bubbles of gas left consisted of nitrogen derived from traces of air in the apparatus (fig. 5), and which had not been removed owing to insufficient sparking. There was no rare gas present. Another sample of the same gas was analysed, with the following result :—

	Per cent.
Carbon dioxide .....	12.11
Carbon monoxide .....	2.20
Silicon hydride .....	86.34
	<hr/> 100.65

The solution in C was evaporated to dryness in a platinum basin, and the equivalent of the ammonium radical in the residue found by estimating the chlorine present.

My thanks are due to Dr. Gwyer for making this analysis, and for assistance in the work on the magnesium and lime residues.

The figures obtained in the analysis were:—

Weight taken.	Chlorine found.	Percentage of chlorine.	
		Found.	In ammonium chloride.
0.2629 grm.	0.1735 grm.	65.99	66.23

The results show plainly that there was nothing but ammonium chloride present.

As Sir William Ramsay has pointed out in his Introductory Note, the negative results obtained in this work do not necessarily indicate that a final end has been reached, they simply indicate the improbability of the existence of a stable elementary gas in the atmosphere with a higher atomic weight than xenon.

My cordial thanks are due to Sir William Ramsay for his suggestions and unfailing interest in the work, in a considerable portion of which he took an active experimental part.

*The Spectrum of Radium Emanation.*

By ALEXANDER THOMAS CAMERON, M.A., B.Sc., and Sir WILLIAM RAMSAY,  
K.C.B., F.R.S.

(Received July 2, 1908.)

In May, 1904, one of the authors, in conjunction with Professor Collie measured the visual spectrum of the emanation accumulated in 14 days from 109 milligrammes of radium bromide, by means of a direct vision spectroscopie.

A subsequent measurement was made with 11 days' accumulation. It was then stated\* :—"The spectrum was very brilliant, consisting of very bright lines, the spaces between them being perfectly dark; it had a striking resemblance in general character to the spectra of the gases of the argon group." This spectrum became rapidly faint, and had largely disappeared in less than a minute; it was replaced by the spectrum of secondary hydrogen.

We have now repeated this experiment several times with the emanation accumulated during 12 days from 477 milligrammes of radium bromide, with partial success; and recently with perfect success, no other spectrum being visible at first but that of the emanation. It was intensely brilliant, and consisted of a number of green, blue, and violet lines, besides a very slightly refrangible line in the red. The spectrum was photographed; but during the exposure, which lasted 4 to 5 minutes, it faded, and was replaced by that of hydrogen. The tube was photographed three times altogether; the second and third exposures lasted about eight minutes; the hydrogen lines, as a rule, were equally strong in the second and third photographs, and almost entirely absent from the first. On reducing the pressure, a number of lines appeared in the second photograph, which seem to be additional lines of the emanation. The action of the discharge is to drive the emanation into the negative electrode, where it is largely absorbed; for the glowing, due to secondary products, was much more brilliant there than through the rest of the tube.

The greater part of the lines previously observed have been confirmed; and a number have been added to the list. The degree of exactitude is of course, very much greater than before; in most cases the limit of error is not greater than one or two Ångström units; the lines of secondary hydrogen already mapped, and apparently not with great accuracy, were taken as fiducial.

\* 'Proceedings,' vol. 73, p. 472.

The secondary spectrum of hydrogen is being re-mapped by Mr. Herbert Watson, and the lines will be corrected as soon as his measurements are complete.\* The following table shows the results of two experiments; in Column 1 are the wave-lengths of the lines; in Column 2 their intensities when photographed during the first experiment; in Columns 3, 4, and 5, their intensities if observed on the first, second, and third photographs of the

Wave-length.	Intensity.			Previous reading.	Remarks.
	Experiment 1.	Experiment 2.		(Ramsay and Collie.)	
6307	—	—	1	1	Probably H.
6070*	0·5	—	8	1	
5995	—	—	1	—	
5887	—	—	3	1	Doubtful Probably H. Uncertain
5584	—	—	1	—	
5077*	—	3	1	—	
4977*	—	3	0·5	—	
4932*	0·5	—	3	0·5	
4926*	—	—	3	—	
4817*	—	2	—	—	
4723*	2	0·5	4	0·5	
4704	—	1	1	—	
4680*	0·5	6	1	—	
4669*	—	2	1	—	Doubtful
4654*	—	2	1	—	
4644*	0·2	8	2	1	
4632*	3	0·5	10	1	
4624*	0·5	8	3	1	
4608*	—	2	7	1	
4603*	2	3	—	—	
4578*	1	2	9	3	
4547	—	1	—	—	
4509*	1	2	4	1	
4505	—	1	—	—	Doubtful
4440	—	1	—	—	
4435*	1	1	3	1	
4310*	2	3	5	—	
4208*	0·5	9	4	3	
4170*	—	10	4	2	
4114*	—	2	—	—	
4057	5	3	15	20	
4014*	—	3	0·5	—	
3977*	—	6	2	—	
3967*	—	5	—	—	Doubtful
3950*	—	2	—	—	

\* The corrected values are given in the addendum, *infra*, all except five lines, for which the corrected values are 6068, 5887·5, 4702, 4634·5, 4058·5.

second experiment. Column 6 gives the wave-lengths and intensities of the lines observed visually by Collie and Ramsay. The photograph taken during the first experiment showed chiefly secondary hydrogen and some nitrogen; it is somewhat remarkable that so many lines belonging to the emanation were photographed.

The asterisked lines are undoubtedly those of the emanation.

The greater number of these lines grow weaker with the duration of the discharge, and in some cases fade out, so that they are absent from the third column of Experiment 2. But in some cases, and conspicuously in line 4058.5, the intensity has increased astonishingly. This line is near a mercury line of wave-length 4047, the intensities of which vary from 3 in the first plate to 6 in the second, and to 2 in the third; it is given in spectrum tables as of intensity 10. It looks probable, therefore, that the line 4058.5 is due to some product of the decay of the emanation, the quantity of which increases with length of passage of the discharge.

Through the kindness of Sir William Huggins, we have been furnished with a list of the more important lines of the nebulae. No one of them appears to be due to radium emanation.

*Addendum.—Received August 5, 1908.*

In the experiments just described ordinary panchromatic plates were used. In two later experiments "spectrum" plates were employed. In the first of these the spectrum only lasted a minute and a-half. The lines in the photograph were all very weak. They included most of the emanation lines previously photographed, together with the slightly refrangible line in the red, already referred to; the wave-length of this line is 7050.

In all these experiments the spectrum tubes were fitted with aluminium electrodes, and the rapid absorption of the emanation was undoubtedly connected with this. In a final experiment, on the recommendation of M. de Bort, we used copper electrodes. The result was entirely satisfactory. They apparently contain no hydrogen, and absorb emanation much more slowly. The tube became vacuous only after 7 to 8 minutes and a very good photograph was taken. It contained a large number of new lines belonging to the emanation spectrum, besides a number of mercury lines. The hydrogen lines were few, and their intensity were unaltered throughout.

The unitalicised figures in the following table refer to lines measured in this last experiment with the corresponding intensities. Italicised figures refer to lines absent in this case, but measured previously.

Wave-length.	Intensity.	Remarks.	Wave-length.	Intensity.	Remarks.
7050	2		4592	1	Doubtful
6150	2		4585	4	Observed before, weak
6101	2		4578 ·5	3	Very strong previously
6055	2		4545 ·5	2	
5980 ·5	2		4541	1	
5879 ·5	2		4532 ·5	2	
5586	2		4524	4	Possibly H.
5446	1		4509	4	
5419	4		4505	2	Doubtful
5370	2		4501	3	
5335	3		4481	4	
5289	6		4463 ·5	8	
5083	2		4449	4	
4979	2		4441 ·5	<1	
4936	2	Possibly H.	4436 ·5	<1	
4920	3	Observed before <1	4416 ·5	4	
4883	2	" " <1	4391	3	
4873	2		4349	6	Observed before
4843 ·5	10	" " <1	4331	4	
4816	2		4307	2	
4806 ·5	1		4246	4	
4768	2	" " weak	4239	3	Observed before <1
4781 ·5	2	" " "	4204	5	
4722	4	" " "	4189	3	
4695 ·5	2	" " "	4167	6	
4681	5		4114	3	
4672	7		4018 ·5	4	
4652 ·5	3		3982	8	
4645 ·5	6		3973	6	
4626 ·5	10		3958 ·5	3	
4616	2		3879 ·5	10	
4610	2		3866 ·5	6	
4606	10		3856 ·5	4	

Since this paper was communicated to the Society Professor Rutherford and Mr. Royds have published a preliminary account of their work on the same subject.\* Their figures show a very close agreement with those given above.

Our thanks are due to Mr. Herbert Watson for some assistance in measuring the wave-lengths of the lines, and for placing at our disposal his results of measurement of the secondary spectrum of hydrogen.

\* 'Nature,' July 9, 1908, p. 220.

*Further Note on a Luminous Glow generated by Electrostatic Induction in an Exhausted Vessel made of Silica.*

By FREDERICK JOHN JERVIS-SMITH, M.A. (Oxon), F.R.S.

(Received June 15,—Read June 25, 1908.)

1. A glow-bulb rotating within a shallow cylindrical inductor made with a dome-shaped end (devised by my son, E. J. Jervis-Smith, R.F.A.), placed symmetrically, with respect to the axis of rotation of the glow-bulb, exhibited the glow and magnetic phenomena described in the former paper and exhibited at the Royal Society on May 13, 1908.

Sir Oliver Lodge has kindly repeated some of my experiments with glass bulbs, as set forth in the former paper, and also surrounded by a ring-shaped inductor, and has produced the same effects.

2. Two bulbs, similar in shape and size to those described in the paper referred to, were made by the Silica Syndicate, London, of pure fused silica. Up to this time (May 30, 1908), as far as I can discover, no highly exhausted tubes of pure silica have been made; but now means have been found whereby such apparatus may be manufactured. The only difficulty which remained was to seal off an exhausted silica tube in such a manner as not to alter the condition of the vacuum by the introduction of hydrogen gas, since at a high temperature hydrogen passes through fused silica. By employing a means of sealing not involving the burning of hydrogen, this trouble may be avoided, if great accuracy is aimed at.

3. The residual gas in the new silica glow-bulbs, after exhaustion to a Röntgen vacuum, was air. A glow-bulb was supported by its stem at the distance of 0.5 cm. from a disc-shaped terminal of an induction coil. Opposite to the bulb and disc, a pointed terminal (negative) was placed at such a distance that sparks did not pass when the point and disc were 10 cm. apart, but only a brush discharge, which played freely over the bulb.

When the coil was in action, the bulb was illuminated with a brilliant emerald green glow. When the discharge was stopped, the bulb continued to glow, the glow slowly dying out in about fifteen minutes. This remarkable after-glow could be easily seen by a person at a distance of 3 or 4 metres from the bulb for the first eight or ten minutes after the excitation of the bulb. In one experiment a bulb showing the after-glow was carried about 80 metres, through a garden, at night; it still retained its glow as it did when not moved in the laboratory.

4. No *glass* glow-bulbs, treated in exactly the same manner, exhibit this after-glow phenomenon in the slightest degree.

5. The silica glow-bulb, when under the influence of the above-mentioned discharge, showed green streaks of glow brighter than that of the whole bulb, slowly moving within the bulb.

6. A silica glow-bulb was mounted in the rotating apparatus described in §(2) of the paper of January 30, 1908. The inductor was charged from about 1800 to 2000 volts. The silica glow-bulb gave out a glow quite unlike that of the glass bulbs described in the former paper. In the experiments with the glass bulbs the glow was not at all strong when the inductor was charged to about 1800 volts; also, the magnetic phenomena could only be seen by some persons at a distance of 0.25 to 0.5 metre from the apparatus; but when a silica bulb, similar in size and exhaustion to the glass bulbs, was rotated, it could be seen without difficulty in the dark at a distance of 5 metres, and when the inductor was charged up to 3000 to 4000 volts it was clearly visible at 15 metres from the glow-bulb.

7. The magnetic phenomena appear to be the same as those which exist when a glow-bulb is employed made of glass.

8. A silica glow-bulb was rotated (as in the previous experiments, by means of a hollow mandrel) with a portion of the bulb in contact with dry mercury, supported under the rotating bulb in a circular wooden dish. On rotating the bulb it was almost instantly filled with a bright greenish glow. The bulb was rotated about thirty times per minute; on increasing the surface velocity of the bulb, so that the mercury was thrown out of the dish, the glow produced was but very slightly increased.

9. A flexible brush of fine copper wire, supported on an insulator, was held in light contact with the bulb, about 1.5 cm. above the surface of the mercury. The brush was connected to a graduated electroscope. When the bulb was rotated, the electroscope was rapidly charged up to 1500 volts; also a Leyden jar was easily charged from the copper brush and insulated conductor.

10. This method of generating electricity placed in one's hands an excellent method of gradually charging a body to any desired degree, from zero up to the highest potential attainable by the arrangement. Owing to the highly insulating nature of silica, practically no leakage back to the bulb through the brush takes place. The sign of the electricity so produced is negative. The brush should in all cases lightly touch the rotating bulb.

11. Solid fused silica was employed, and electricity was generated as in (10), but only the slightest trace of light was visible.

12. A jet of mercury, falling through 4 cm., was made to play upon the surface of a silica glow-bulb, when it instantly became luminous. On connecting the point of impact of the drops of mercury with the electroscope,



it was at once charged, as in Experiment 9. The same was the case when solid silica was employed, but hardly any luminosity appeared.

13. All these experiments were repeated with glass glow-bulbs, but the effects were minute in comparison with those produced when silica was used, and it was found that considerable leakage back of a charge took place when glass was used.

14. An electrical machine is now being constructed by me, in which silica and mercury will be used on a far larger scale than in the experiments described in this paper.

I wish to thank Mr. H. G. Lacell, of the Silica Syndicate, for the great care with which the glow-bulbs have been prepared under his supervision.

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### *On the Atomic Weight of Chlorine.*

By EDWARD C. EDGAR, D.Sc., Assistant Lecturer in Chemistry in the University of Manchester.

(Communicated by Professor H. B. Dixon, F.R.S. Received and Read  
June 25, 1908.)

(Abstract.)

Six years ago Professor Dixon and I began a research with the object of determining directly the weight of chlorine which combines with the unit weight of hydrogen. Our method was to burn a jet of hydrogen in an atmosphere of chlorine; hydrogen being stored and weighed in palladium, the chlorine being condensed and weighed as liquid. The number we obtained for the combining weight of chlorine was appreciably higher than that found indirectly by Stas, and still higher than that approved by the International Committee on Atomic Weights.

While this research was in progress, other determinations had been made bearing on the relative weights of silver, chlorine, and nitrogen, so that some modification in the accepted values of one or more of these elements appeared inevitable. The direct "joining up" of the two ends of the chain connecting hydrogen with chlorine thus became a matter of immediate importance. Since the method of burning one gas in an atmosphere of the other had been proved to be accurate within fairly narrow limits, I was encouraged to continue the investigation, and to modify the apparatus, with a view to

eliminate some of the possible sources of error in the former series of experiments.

The most important source of error lies in the weighing of the hydrogen. To diminish this error the weight of hydrogen employed was doubled; and since Professor Dixon and I found, when water was used to condense the hydrogen chloride formed in the flame, that some of the water vapour was decomposed by the free chlorine, I avoided this by burning a jet of chlorine in dry hydrogen, condensing the hydrogen chloride as it was formed in a tube dipped into liquid air. In some of the experiments the hydrogen chloride formed has been weighed. My experiments (concluded in 1907) agree closely with the results previously obtained in 1905. The method employed was briefly as follows:—

Hydrogen, made by the electrolysis of barium hydrate solution, and dried by potash and phosphorous pentoxide, was occluded, and weighed in palladium contained in a boro-silicate glass bulb. The chlorine, prepared by electrolysing fused silver chloride in a Jena glass vessel, was weighed as a liquid in a thick-walled boro-silicate glass bulb. Two ground joints attached these bulbs to a quartz combustion vessel, which was also connected with a vertical quartz tube, and with a steel bomb and a pump. After a thorough evacuation of the whole apparatus, the vertical limb of the combustion vessel was immersed in liquid air. Then the vacuous vessel was filled with hydrogen from the heated palladium bulb. Chlorine was ignited by a spark at the tip of a quartz jet, and continued to burn in the atmosphere of hydrogen with a fine needle-shaped flame. The endeavour was made so to regulate the gases as to maintain the flame until nearly all the chlorine weighed had been burnt. Then the supply of hydrogen was cut off. As the atmosphere became more attenuated the flame died away until, just before it went out, the chlorine was turned off. The hydrogen chloride, immediately after it was formed in the flame, was condensed as a snow-white solid by the liquid air surrounding the vertical limb of the combustion vessel; and a little chlorine, which had escaped burning, was also solidified. At the end of the combustion, the residual gas was extracted by the pump and analysed; it proved to be practically pure hydrogen.

Then the snow-white hydrogen chloride was allowed to evaporate. By passing the gas through a quartz tube filled with mercury vapour, the chlorine it contained was completely removed and the purified hydrogen chloride passed on to a steel bomb immersed in liquid air, where it was condensed in six experiments and successfully weighed in three; in the other three the bomb leaked. In two other experiments the gas was absorbed by water and weighed as aqueous acid. The weights of hydrogen and chlorine burnt were

obtained by subtracting from the total weight of each used the weight of hydrogen extracted by the pump and the weight of chlorine caught by mercury vapour respectively.

The balance was specially made for this work by Oertling; even under the load of the steel bomb, weighing over 1000 grammes, it gave very reliable readings. Each piece of apparatus weighed was tared with another of the same material and of very nearly equal volume and weight, and the small weights used in the weighings were reduced to a vacuum standard.

Below are set out the corrected weights of hydrogen and chlorine burnt in eight experiments, and the weights of hydrogen chloride caught in five:—

	Hydrogen burnt, in grammes.	Chlorine burnt, in grammes.	Hydrogen chloride caught, in grammes.	$\frac{\text{Chloride burnt}}{\text{Hydrogen burnt}}$	$\frac{\text{Hydrogen chloride caught} - \text{Hydrogen burnt}}{\text{Hydrogen burnt}}$
1	2·1452	75·5026	77·6469	35·196	35·196
2	2·0387	71·7504	73·7880	35·194	35·194
3	1·7782	62·5004	—	35·188	—
4	1·9985	70·1638	72·1565	35·196	35·196
5	1·6469	57·9671	—	35·198	—
6	2·1016	73·9662	—	35·195	—
7	1·7254	60·7162	62·4401	35·190	35·189
8	2·0885	73·4991	75·5859	35·192	35·191
Mean.....				35·194 $\pm$ 0·0008	35·193 $\pm$ 0·0009

If the atomic weight of hydrogen be taken as 1·00762, the mean values for the atomic weight of chlorine, calculated from the numbers in the table above, are  $35·462 \pm 0·0008$  and  $35·461 \pm 0·0009$ .

Dixon and Edgar, burning hydrogen in chlorine, found the equivalent of chlorine to be  $35·463 \pm 0·0019$  from their nine experiments.

The concordance of the two sets of experiments is thus exceedingly close, and the number 35·462 may be taken as representing the result of the whole work.

On the other hand Noyes and Weber,\* by passing a known weight of hydrogen over weighed potassium chlorplatinate, noting the loss in weight of the salt, and condensing and weighing in water the hydrogen chloride formed, have recently obtained for the atomic weight of chlorine the mean number  $35·452 \pm 0·0008$  ( $H = 1·00762$ ).

In view of the promised recalculation of the atomic weights by the International Committee this year, I have not attempted to correlate my results with the recent determinations of silver, nitrogen, and chlorine.

\* 'Journal of the American Chemical Society,' vol. 30, p. 13, 1908.

*The Supersaturation and Nuclear Condensation of Certain  
Organic Vapours.*

By T. H. LABY, B.A., Emmanuel College, Cambridge, Exhibition of 1851  
Science Research Scholar of the University of Sydney, Joule Student of  
the Royal Society.

(Communicated by Prof. J. J. Thomson, F.R.S. Received April 10,—Read  
April 30, 1908.)

(Abstract.)

The condensation of drops, which takes place when dust-free air saturated with an organic vapour is cooled by an adiabatic expansion, is the subject of this investigation. The experiments were made with the air and vapour (1) in their natural state, (2) ionised by Röntgen rays.

The apparatus used was in principle the same as that of Mr. C. T. R. Wilson in his experiments with water vapour. The essential part of it is an expansion chamber in communication with a glass cylinder, in which a gas-tight piston slides freely. When a trigger is pulled the piston descends, and a very rapid (adiabatic) expansion of the air and vapour is obtained. The expansion was determined from the initial and final readings of a pressure gauge. The illumination of the expansion chamber was such as enabled any drops formed by the expansion to be readily seen. The liquids used in the experiments were carefully purified.

When the air and vapour are expanded adiabatically their temperature falls, and the pressure of the vapour at this lower temperature is greater than that which it has over a plane surface of the liquid at the same temperature. This supersaturation, however, may not cause the condensation of drops in dust-free air. Expansions of increasing magnitude were made until condensation took place, and then the least expansion required to produce condensation for the conditions of the experiment was determined.

In another series of experiments the expansion chamber was so made that in one part of it the positive ions produced by Röntgen rays were in excess, and in the other adjacent part the negative were in excess; the expansion was identical in both and the result of it could be observed in the two parts simultaneously. In this way the relative efficiencies of the ions as condensation nuclei could be examined.

The results of the investigation may be summarised as follows:—

(1) The least expansion, which causes condensation in air initially saturated with an organic vapour and ionised by Röntgen rays, has been

determined for five esters, six acids (formic to iso-valeric), and iso-amyl alcohol.

(2) In the case of acetic acid the expansion required was greater for feeble Röntgen rays than for more intense ones.

(3) The supersaturation,  $S$ , existing at the end of each of the expansions mentioned in (1) has been calculated, and also for four alcohols and chloroform from Przibram's experiments.

(4) The acids are found to have the largest values of  $S$  and the alcohols the least. The isomers examined have the same value for  $S$  with one exception. In the case of the alcohols, ethyl to iso-amyl, a fairly regular decrease in  $S$  accompanies the addition of a  $\text{CH}_2$  group.

(5) The existing theory of condensation on ionic nuclei has been given, values of  $S$  have been calculated from it, and compared with  $S$  deduced from the observed expansions. The agreement in the case of acetic, propionic,  $n$ -butyric, and iso-butyric acids, and methyl alcohol is very close.

(6) The expansion and supersaturation necessary for condensation on the natural nuclei have been determined for the same (dust-free) vapours. In the case of formic, acetic, and butyric acids a distinctly greater expansion is required to catch the natural nuclei than that required for the ionic nuclei produced by Röntgen rays.

(7) As the expansion was increased the number of drops usually increased continuously with it so that the fog point was ill defined, except in the case of tertiary amyl alcohol.

(8) Ethyl acetate, methyl butyrate, propyl acetate, acetic acid, and iso-amyl alcohol were found to condense for a smaller expansion on the positive nucleus than on the negative. Water is the only known substance for which the negative ionic nucleus is more efficient than the positive.

(9) On bubbling air through methyl, ethyl, and iso-amyl alcohols, ethyl acetate, propyl acetate, methyl butyrate, chloroform, and ethyl iodide they became negatively electrified. This was the sign of the electrification to be expected from Professor Thomson's double layer theory of the relative efficiency of ionic nuclei. Acetic acid was not in agreement with the theory for it became positively charged on bubbling.

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*The Electrical Qualities of Porcelain, with special reference to Dielectric Losses.*

By H. F. HAWORTH, Ph.D., M.Sc., B.Eng., Assoc.M.I.E.E.

(Communicated by Professor W. E. Ayrton, F.R.S. Received May 7,—  
Read June 4, 1908.)

The following research was undertaken to determine some of the electrical properties of porcelain, and their variations with respect to potential, temperature, and time.

The electrical properties investigated in this paper are as follows :—

*A. Capacity Measurements.*

1. The rate of charge of a porcelain condenser.
2. The charge of a porcelain condenser as a function of the potential.
3. The influence of sudden cyclical changes of potential on the charge of a porcelain condenser.
4. The dielectric constant of porcelain as a function of the temperature, and its value.

*B. Conductivity Measurements.*

5. The apparent conductivity of porcelain as a function of the potential.
6. The apparent conductivity of porcelain as a function of the time of electrification.
7. The apparent conductivity of porcelain as a function of the temperature, and its value.

*C. Dielectric Loss Measurements.*

8. Contact method, variable frequency, and constant potential.
9. Thermo-electric method: Constant frequency, variable potential.
10. Thermo-electric method: Variable frequency, constant potential.
11. Historical.
12. Summary.

*Material.*—The porcelain was in the form of glazed discs, about 21 cm. in diameter and 0.55 cm. thick, from the Fabrik Hermsdorf, Sachsen-Altenburg. The discs had a circular tinfoil electrode of 20.5 cm. diameter fixed on them on each side.

*Instruments.*—Current readings were taken with a Siemens and Halske galvanometer, the usual sensibility of which was about  $0.5 \times 10^{-10}$  ampere

per millimetre deflection at 2 metres. The deflections were read by means of a telescope and scale, and could be estimated to 1/10 mm.

*Batteries.*—For potentials up to 200 volts a battery of 100 large accumulators was used. For potentials up to 5000 volts a battery of 2500 small accumulators was used. These cells were made up in sections of 50 in two rows of 25 each, fixed into a paraffin wax base which rested on a glass plate backed with wood. Contact was made with mercury cups.

1. The rate of charge of a porcelain condenser.

Two plates connected in parallel were used, and they were charged and discharged by means of a paraffin wax insulated mercury switch.

To secure accuracy, and to avoid temperature and other effects, the following method was adopted:—

(1) The plates were charged for one second, and were then discharged through the galvanometer, the swing being noted.

(2) They were then charged for two seconds, discharged, and the swing noted. The plates were discharged for a time equal to, or greater than, the charge time.

About 70 of these double readings were taken, the charges of one and two seconds alternating. The averages of these results were then calculated, and from their difference the percentage increase of charge, when the charge time was increased from one to two seconds, was calculated.

The charging voltage was also noted, and then we have two points on the time-charge curve for this particular voltage.

The plates were then charged for two and three seconds in the same manner, then for three and four seconds, four and six seconds, etc.

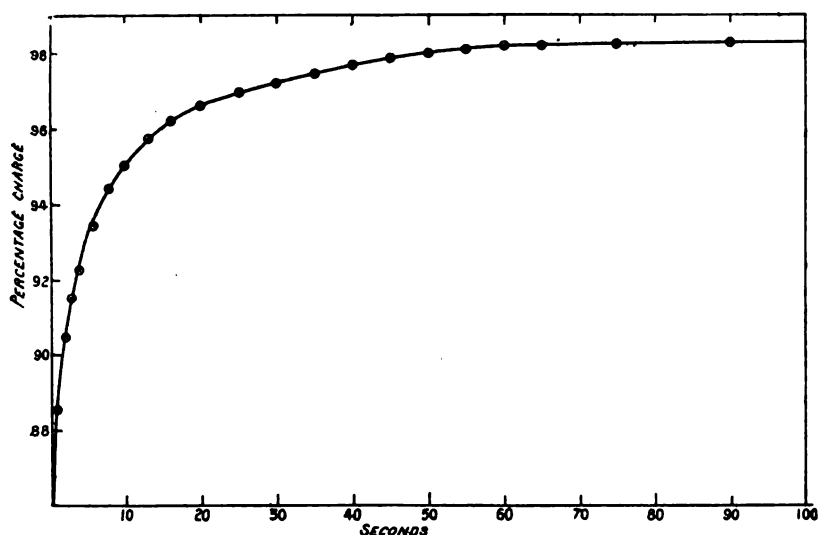
It was assumed in this experiment, and proved in the next, that the potential charge curve for porcelain was a straight line, therefore the time-charge curve may be continued, and the charge for three seconds calculated for the original voltage.

The curve was continued in this manner up to 30 minutes' charge. Beyond 90 seconds a slight increase of the charge will be noted, for this may be due to a temperature effect; practically the porcelain is fully charged in one minute, if we take the first galvanometer swing as a measure of the capacity. The results are graphically represented in Curve 1, and numerically in Table I.

In the 20 and 30 minute charges the readings varied somewhat, it was thought on account of temperature changes; so some rough temperature readings were taken, and the variations in swing were reduced to percentages per degree centigrade, the average result being 1.9 per cent.

Table I.

Charge time, seconds.	Percentage charge.	Charge time, seconds.	Percentage charge.
1	88.58	35	97.41
2	90.50	40	97.62
3	91.54	45	97.82
4	92.29	50	97.96
6	93.44	55	98.07
8	94.45	60	98.11
10	95.08	65	98.13
13	95.79	75	98.26
16	96.21	90	98.28
20	96.60	600	98.68
25	96.95	1200	99.57
30	97.15	1800	100.00



CURVE 1.—Charge of a Porcelain Condenser as a Function of the Time of Charge.

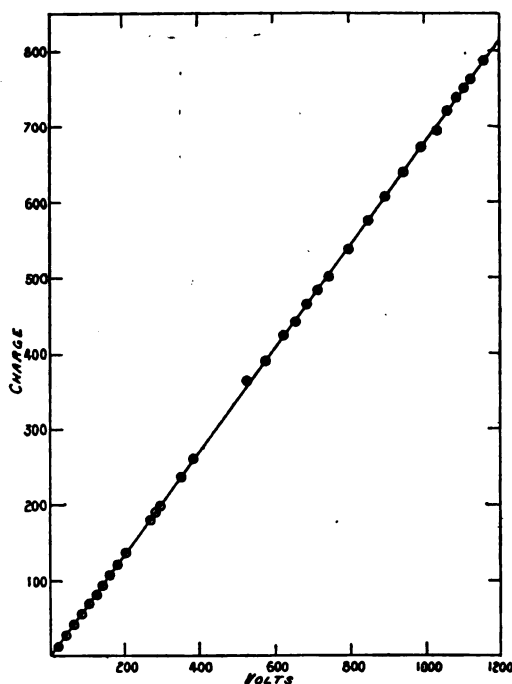
## 2. The charge of a porcelain condenser as a function of the potential.

The two plates used in the previous experiment were charged for half a minute, discharged for one minute, and the swing of the galvanometer and the potential were noted.

Readings up to 200 volts were taken in steps of 20 volts, and 40 readings were taken at each voltage. Temperatures were noted at the beginning, middle, and end of each series, and a rough estimate of the percentage variation of charge per degree centigrade was made; it was about 2.3 per cent. Up to 200 volts the points lie along a straight line, and any small variations from it followed the temperature variations.



The potential charge curve was now constructed, using the high-tension battery up to 1200 volts. The results are plotted in Curve 2, and from it will be seen that the charge is directly proportional to the charging potential. This agrees with J. Curie's work on crystals,\* in which he found that the charging current is exactly proportional to the potential when the potential changes are slow. It will be seen later that this does not hold if the changes are rapid.

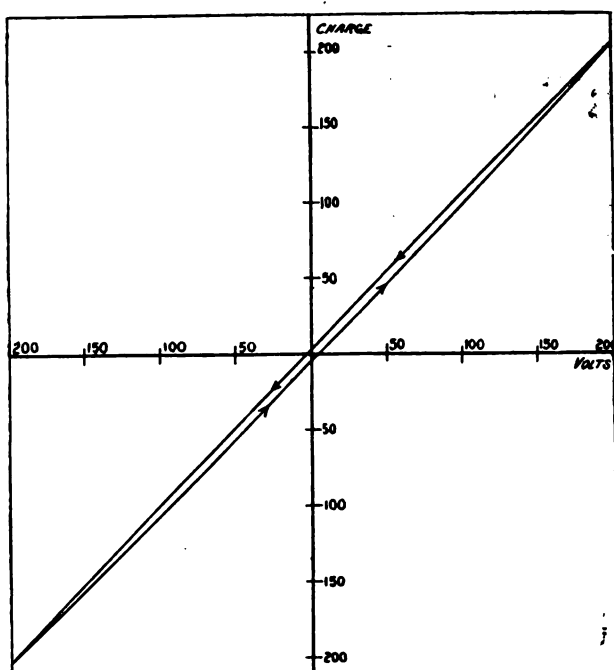


CURVE 2.—Potential-Charge Curve for Porcelain Condenser.

3. The effect of sudden cyclical changes of voltage on the charge of a porcelain condenser was now investigated.

Three plates were enclosed in a vessel, containing phosphoric acid as drying agent, and were charged, and discharged, for one minute in the usual manner. The charging potential was altered by approximately 40 volts each time between limits  $\pm 200$  volts. Several cycles were gone through, and the charge was plotted against potential in Curve 3. The descending values are slightly greater than the ascending ones, thus showing a small dielectric loss even with very slow rates of change of the field. This point is dealt with more fully under the heading "Dielectric Loss."

\* J. Curie, 'Thèse de Doctorat,' June, 1888.



CURVE 3.—Potential-Charge Curve for Porcelain Condenser, Potential varied cyclically.

4. The variation of the dielectric constant with temperature was investigated in the following manner :—

Three porcelain plates were placed in a copper vessel containing a drying agent. This copper vessel was heated by means of an oil bath, the oil of which was first heated to the required temperature by a Bunsen burner. The temperature was then maintained constant by means of an electric heater, which consisted of a framework of asbestos insulated iron wire wound on the inner copper vessel. The heat radiation from the apparatus was exactly balanced by the current sent through the resistance framework.

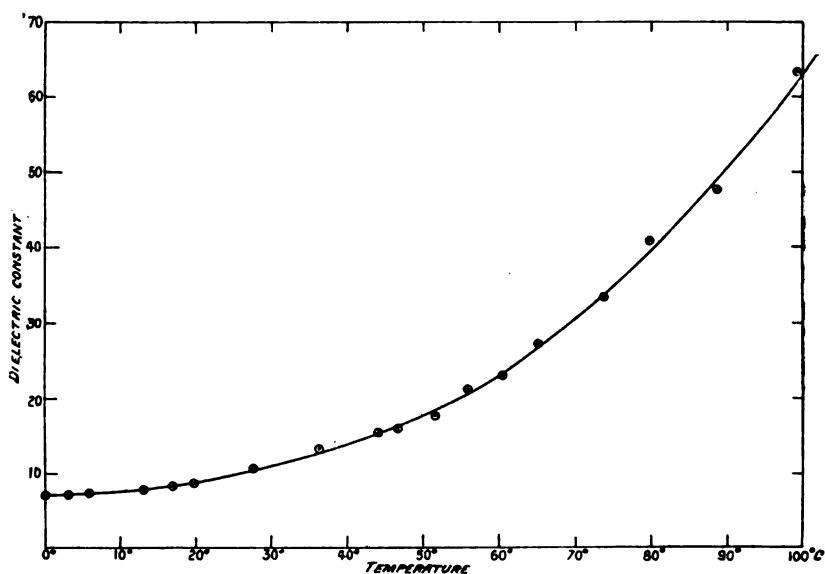
The oil was circulated by means of a pump and stirrers worked by hand.

The temperature was measured by a thermometer resting on the porcelain. The porcelain was charged and discharged in the usual manner, charge and discharge being each of one minute's duration, the potential being reversed each time to neutralise polarisation effects. The charging and discharging was continued until the galvanometer swings and temperature were constant for at least one hour.

The results of the experiment are given in Table II, and are graphically shown in Curve 4.

Table II.

Temperature, °C.	Dielectric constant.	Temperature, °C.	Dielectric constant.
0·38	7·22	46·66	16·00
3·44	7·48	51·59	17·95
5·93	7·53	55·93	21·20
13·17	7·95	60·50	23·00
16·52	8·60	65·00	27·30
19·92	8·95	73·89	33·20
27·55	10·82	79·88	40·80
36·22	13·40	88·56	47·50
44·04	15·50	99·00	63·50



CURVE 4.—The Dielectric Constant of Porcelain as a Function of the Temperature.

From the results it will be seen that the temperature has a very great influence on the dielectric constant.

At temperatures 0° to 30° C. the increase of capacity is much smaller than at higher temperatures. Between 0° and 30° the capacity increases 54 per cent. (0·0006 microfarad), and between 70° and 100° it increases 108 per cent. (0·0052 microfarad), being a nine times as great a rate of growth. From 0° to 30° the dielectric constant is a quadratic function of the temperature, the equation being of the form—

$$C_t = C_0(1 + 0·00223t + 0·0005t^2).$$

where

$C_t$  = dielectric constant at temperature  $t$

and

$C_0$  = dielectric constant at zero temperature.

From 30° to 100° the equation of the curve is

$$C_{t_1} = C_{t_2} e^{0.0264 (t_1 - t_2)},$$

where  $C_{t_1}$  = dielectric constant at temperature  $t_1$

and  $C_{t_2}$  = " " " "  $t_2$ .

From Table II, and the above equation, we find that the dielectric constant for this kind of porcelain at 20° C. is 8.95.

### *B. Apparent Conductivity Measurements.*

By the apparent conductivity is meant the conductivity as expressed by the ratio of current to potential.

#### 5. The apparent conductivity of porcelain as a function of the potential.

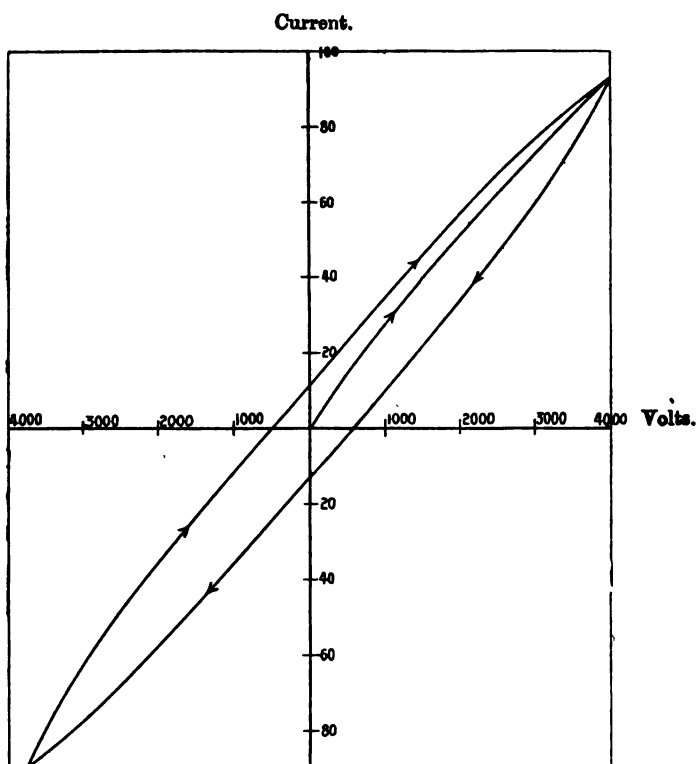
A porcelain plate was placed in an air-tight glass vessel containing a drying agent, and a current was sent through it as well as through the galvanometer from the high-tension battery. At the end of 1½ minutes the deflection was noted, and from it the conductivity per centimetre cube was calculated.

The potential was increased by steps of 110 volts to 2500 volts; the current curves obtained were concave towards the voltage axis, but they did not remain constant, they varied daily. The conductivity decreased greatly with increase of potential.

On taking the readings with decreasing potentials the results obtained were widely different from those obtained with increasing potentials, and on putting the porcelain through a cycle of electrification the curve obtained for current with respect to the potential formed a closed curve as shown in Curve 5.

On putting the porcelain through a number of continuous cycles of electrification the same curve was traced out each time, thus showing that a steady cyclical state had been reached. The porcelain, on having a potential impressed on it, generates a back E.M.F. which varies for different cycles of electrification. In other words the dielectric becomes polarised.

If we consider the dielectric as being made up of electric doublets (particles of matter having electric poles), they are normally in a heterogeneous condition, but when an electrostatic field is impressed on the dielectric, the particles tend to orientate with their electrical axes along the lines of force. The number which would do so would vary directly with the impressed voltage, and their electrostatic potentials would add up to resist the flow of current through the dielectric. The free poles of the particles in contact with the electrodes would constitute the charge.

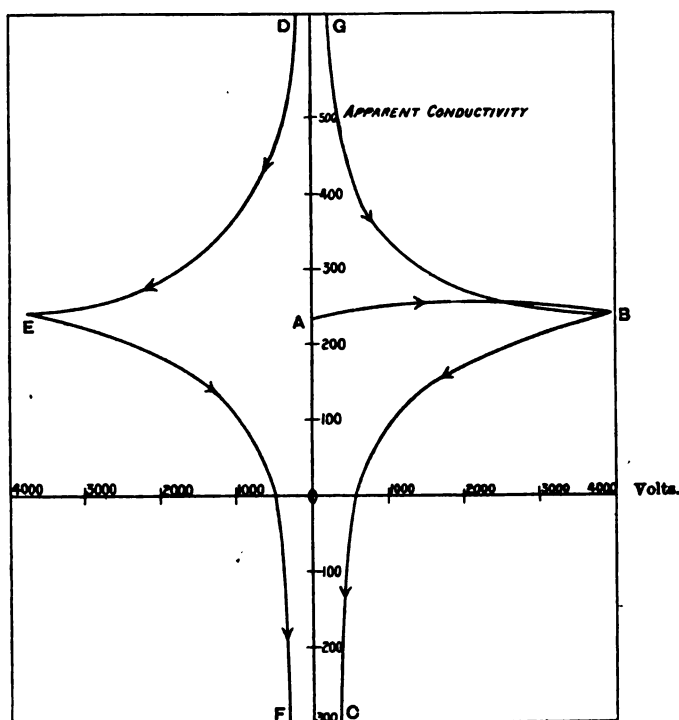


CURVE 5.—The Current-Potential Curve for Porcelain, the Potential being varied cyclically.

On Curve 6 the apparent conductivity is plotted with respect to the potential. It will be noticed that on starting with an unpolarised dielectric, the conductivity is fairly constant for increasing potentials (A to B), but on decreasing the potential the conductivity rapidly falls owing to the polarisation of the dielectric (B to C), and the fact that the curve goes off to a negative infinity simply means that the back E.M.F. of the porcelain is greater than the impressed E.M.F. The curve starts again from  $+\infty$  on account of the back E.M.F., then assisting the forward E.M.F. The conductivity then decreases more slowly (D to E), reaching a fairly level value at the position of maximum E.M.F., and on decreasing the E.M.F. it goes through a negative infinity again (E to F), starting again from positive infinity (G).

A similar curve would be obtained if we plotted the reluctance of an iron circuit against the magnetomotive force.

Current voltage curves were plotted for cycles  $\pm 4000$ ,  $\pm 3000$ , and  $\pm 2000$  volts with similar results.



CURVE 6.—Apparent Conductivity-Voltage Curve for Porcelain.

The back E.M.F.'s for zero current, *i.e.* the points where the curves cut the voltage axes, were as follows:—

±4000 volts curve.....	+550 and -540 volts,
±3000       "       .....	+450   "   -420   "
±2000       "       .....	+340   "   -320   "

It will be noticed that the positive values are always greater than the negative ones. The averages of these back E.M.F.'s bear the following relationship to one another:—

$$V_{4000} : V_{3000} : V_{2000} :: 1.65 : 1.31 : 1.00.$$

The back E.M.F. is not proportionate to the voltage applied. It would seem as if the number of doublets coming into line per unit fall of potential was decreasing, or in other words the permeability of the dielectric decreases with increase of electrification, or the dielectric tends towards electrical saturation.

The currents with no applied voltage, *i.e.* the points where the curves cut the current axis, were as follows:—

±4000 volts curve.....	+12.0 and -12.5 volts,
±3000       "       .....	+11.0   "   -12.0   "
±2000       "       .....	+ 8.0   "   - 9.0   "

The negative values are greater than the positive ones. The current due to the polarisation of the dielectric does not increase proportionately to the amplitude of the cycle but varies with the back E.M.F.

The currents at  $\pm 4000$ ,  $\pm 3000$ , and  $\pm 2000$  volts were:—

$C_{4000}$ ..... + 93 and - 98,

$C_{3000}$ ..... + 80 „ - 88,

$C_{2000}$ ..... + 54 „ - 56.

The apparent conductivity increases with decrease of voltage. The negative values here are greater than the positive, the sum of these variations being that the current curves are depressed slightly into the negative quadrants.

6. The variation of the apparent conductivity of porcelain with the time of electrification was now investigated.

Fifteen plates, connected in parallel, were placed in a glass vessel containing a drying agent and a thermometer. The plates were placed in a pile on porcelain feet and were connected in parallel with strips of tinfoil. The glass vessel was sealed up with paraffin wax, and the connecting wires were brought out through long glass tubes filled with paraffin wax. Current was supplied by a battery of 100 cells, the voltage being constant (200) throughout the experiment.

The apparent conductivity plotted against the time gave Curve 7 (A), from which it will be seen that the conductivity falls very rapidly in the first 10 minutes, and then more gradually for an hour. After 18 hours the conductivity was considerably smaller than at the end of the first hour, and after 65 hours the conductivity had an intermediate value. This was probably a temperature effect. After 65 hours 35 minutes the electrodes were short-circuited through the galvanometer; a large current was given in the reverse direction which was much greater than the positive current measured before switching the cells off. This was not the ordinary capacity discharge, as the galvanometer was short-circuited while this was taking place. This current was measured every minute for over two hours, and it fell in the same manner as the current produced by the applied E.M.F. fell. The results are shown graphically in Curve 7 (B); they indicate that the dielectric takes a very considerable time to polarise completely, and that in doing so it stores up energy which may afterwards be returned. The cycle is reversible, the porcelain dielectric acts like an accumulator. From the above result it would appear that the current voltage loops of the previous experiment would alter with the time of the cycle, turning in a clockwise

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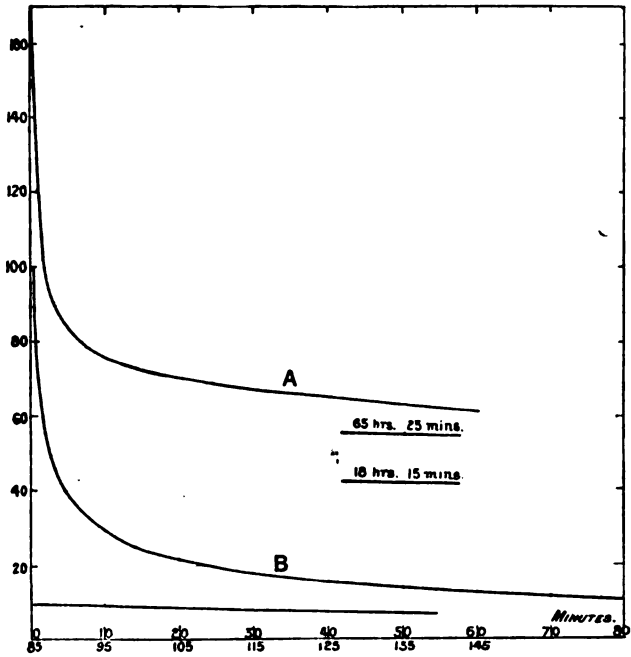
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CURVE 7.—A. Conductivity of Porcelain as a Function of the Time of Electrification.  
B. Short Circuit Current from Porcelain.

direction with increased time of the cycle on account of the lower conductivity due to the increase of polarisation with time. This point was investigated with the 15 plates and the 200-volt battery.

The voltage was raised or lowered by steps of 40 volts each time. The time of the step in the first series was one minute, for the second series two minutes, for the third series three minutes, fourth series five minutes, fifth series seven minutes.

The curves flatten out and turn in a clockwise direction as the time of the cycle increases.

The areas of the loops bear the following ratio to one another:—

$$A_1 : A_2 : A_3 : A_5 : A_7 :: 171 : 146 : 126 : 122 : 100.$$

The maximum currents bear the following ratio:—

$$C_1 : C_2 : C_3 : C_5 : C_7 :: 158 : 150 : 141 : 120 : 100.$$

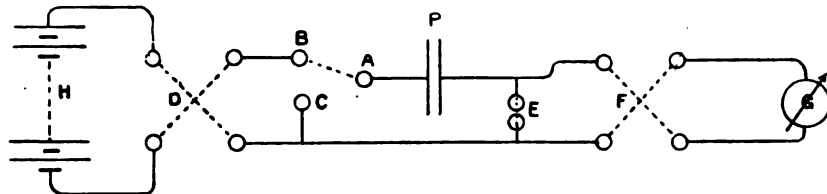
The apparent conductivity has decreased with the increased time of the cycle, thus showing viscosity in the conducting mechanism.

7. The conductivity of porcelain as a function of the temperature.

Fourteen porcelain plates were placed in a pile in the inner copper vessel used in the previous temperature experiment, with phosphoric acid as drying



agent. The heating arrangements were as before, but the oil was maintained at a uniform temperature by an inclined propeller driven by a small motor. The plates were connected in parallel by strips of tinfoil, and the terminals consisted of two mercury cups into which dipped glass tubes which passed through air-tight holes in the cover of the vessel. The mercury excluded air from the vessel, and contact was conveniently made with the porcelain by dipping wires into the mercury. Leakage was tested for by just lifting the wires out of the mercury and noting the deflection. In all cases, however, the leakage was practically *nil*. The top and bottom porcelain plates had no electrodes and simply served as insulators. The connections were as follows :—



H. Charging battery. D. Battery reversing switch.

E. Galvanometer short-circuiting switch.

F. Galvanometer reversing switch.

P. Porcelain.

A B C. Charging and discharging switch.

By connecting A to B current was sent through the porcelain, and by connecting A with C the porcelain was discharged.

The conductivity was measured after one minute's electrification by opening the short-circuiting switch E and noting the first swing.

The porcelain was then discharged for four minutes to get rid of polarisation; the battery and galvanometer connections were reversed, and the conductivity was again measured with the reversed potential. At each reading the temperature of the porcelain was noted, and when both galvanometer swing and temperature had been steady for at least one hour, the average of these readings was taken and the conductivity calculated. The porcelain was usually heated for five or six hours before taking the final readings, as it took a long time to reach a steady electrical state corresponding with a steady temperature.

The results of the experiment are given in Table III and Curve 8. It will be seen that the increase of conductivity with temperature is very great. The following is the equation for the curve :—

$$\gamma_t^* = \gamma_{t_1} \cdot e^{0.090837(t_1 - t_2)},$$

where

$\gamma_{t_1}$  = conductivity at temperature  $t_1$

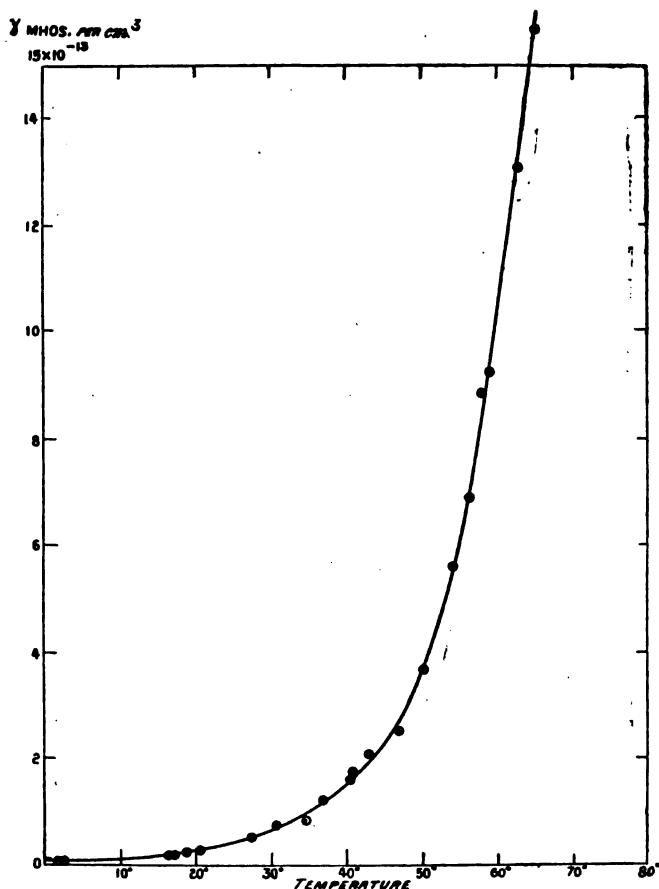
and

$\gamma_{t_2}$  = " " " "  $t_2$

From Table III and the above equation the specific conductivity of porcelain, calculated at 20° C., was  $0.2624 \times 10^{-13}$  mhos per centimetre cube.

Table III.

Temperature, ° C.	Specific resistance, ohms per cm. <sup>3</sup>	Temperature, ° C.	Specific resistance, ohms per cm. <sup>3</sup>
1.68	$143.0 \times 10^{13}$	40.86	$5.70 \times 10^{13}$
2.10	141.0 "	43.03	4.85 "
16.40	51.5 "	47.00	4.01 "
17.00	50.8 "	50.40	2.64 "
18.65	42.8 "	54.01	1.78 "
20.50	35.5 "	56.51	1.44 "
27.32	20.0 "	58.04	1.11 "
30.87	14.0 "	59.12	1.08 "
34.70	11.8 "	62.72	0.77 "
37.03	8.24 "	64.89	0.64 "
40.62	6.25 "	81.93	0.15 "



CURVE 8.—Apparent Conductivity of Porcelain as a Function of the Temperature.

$$\gamma_1 = \gamma_2 \cdot e^{0.080837(t_1 - t_2)}$$

C. *The Dielectric Loss.*

8. The foregoing results show that there is a loss of energy in putting a porcelain condenser through a cycle of electrification, and it is desirable to find on what factors this loss depends and the laws connecting it with variations of voltage, frequency, and temperature. Another point which suggests itself is: Does the capacity of the condenser alter under electrostatic pressure, and if so, how?

To investigate the dependence of the dielectric loss on the frequency of the cycle of electrification, the following experiments were made:—

A porcelain plate was placed in a sealed glass vessel, with sulphuric acid as drying agent, and was connected across the secondary of a transformer giving about 2000 volts. The current and voltage waves were then plotted with the Joubert contact method. The area of the current wave was then calculated for different values of the time, and so the quantity of electricity on the condenser was obtained for that time,  $Q = \int idt$ .

The voltage at this time was known from the voltage curve, and  $Q$  was plotted against  $V$ . The resultant curve enclosed an area similar to Curve 3. The area of this curve represents the energy required to put the condenser through a cycle of electrification at that particular frequency and voltage.

A number of these curves were constructed at various frequencies, and the results are given in Table IV. These results seem to show that the loss per cycle is roughly a constant quantity. Results 7, 8, and 9 vary considerably from the average. This may be due to errors of measurement, also the process of obtaining the final loss curve is rather a complicated one, and errors could easily creep in.

Table IV.

Cycles per second.	$V_{\max}$ .	Loss per cycle. Joule $10^{-4}$ .	Temp., ° C.
Part I (for whole plate).			
107	3000	8.83	22.4
114	2760	8.30	23.5
130	2680	9.45	19.8
140	3060	7.80	20.8
150	2950	9.55	20.0
160	2960	9.20	22.1
170	3020	14.8	20.6
180	2685	29.8	18.9
190	3000	12.3	18.5
200	2960	9.45	20.3
Part II.			
110	2580	5.5	
125	2640	4.98	
150	2500	4.57	
175	2580	5.57	
225	2600	7.58	

To investigate these points further, the following method was adopted, which could be worked more rapidly, and by one person alone, whereas the previous method required two observers.

The porcelain plate was placed in a large glass case containing some strong sulphuric acid. Pressure was supplied with a Ferranti transformer, transforming from 150 to 40,000 volts.

In series with the porcelain condenser was placed a condenser of large capacity ( $C_1$ ) compared with that of the porcelain ( $C_2$ ), and a non-inductive resistance of 40,000 ohms. The current through the porcelain was measured by measuring the voltage across the resistance, and the voltage across the porcelain was measured by the same instrument (an Ayrton and Perry Quarter Cylinder Electrometer) being placed across part of a non-inductive resistance, which itself was placed across the primary of the transformer (see diagram of connections). Connection to the bottom electrode of the porcelain was made through the brass case of the thermopile. The current passing had no effect on the thermopile.

It was intended to measure the capacity of the porcelain ( $C_2$ ) by measuring the pressure across the condenser ( $C_1$ ) placed in series with it, according to the law  $C_1 V_1 = C_2 V_2$ , where  $V_1$  being small the capacity  $C_1$  could be assumed to remain constant, but on connecting the condenser  $C_1$  to the electrometer a small deflection was first obtained which rapidly grew larger until it was beyond the range of the electrometer. It was found that this deflection was due to polarisation, for, when a battery was placed in series with the electrometer, the deflection always increased when the negative pole of the battery was connected with the earthed side of the condenser, thus showing that the polarising current was passing through, or over, the porcelain from low to high tension side. It was thought that perhaps the brush discharge was causing this effect, so an earthed guard ring was put round the bottom electrode, but the result was the same. This condenser was then dispensed with, and capacity calculations were made from the values of the current, voltage, and frequency. This was allowable as the E.M.F. wave was a pure sine wave.

A considerable alteration had to be made in the apparatus on account of the large quantities of ozone and oxides of nitrogen which were formed by the brush discharge, and which rendered the rooms very objectionable to work in. The porcelain plate was placed on one end of a thermopile (used for temperature measurements), the whole standing in a large photographic dish, and was covered with a bell-jar.

Air was sucked into the apparatus through two towers containing calcium chloride, and a wash-bottle containing sulphuric acid (see diagram of

apparatus). The bell-jar was sealed at the bottom with ordinary machine oil. The ozonised air was led out through a tower containing manganese dioxide (to split the ozone up into oxygen), and a wash-bottle containing strong sulphuric acid, to prevent any water vapour from creeping into the apparatus. The air current was produced by an ordinary filter pump, and the air was dried before entering the apparatus, in order to diminish the brush discharge.

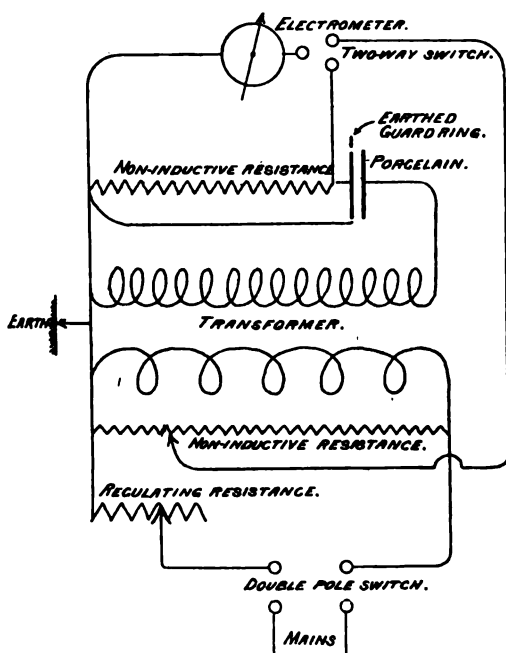


Diagram of Connections.

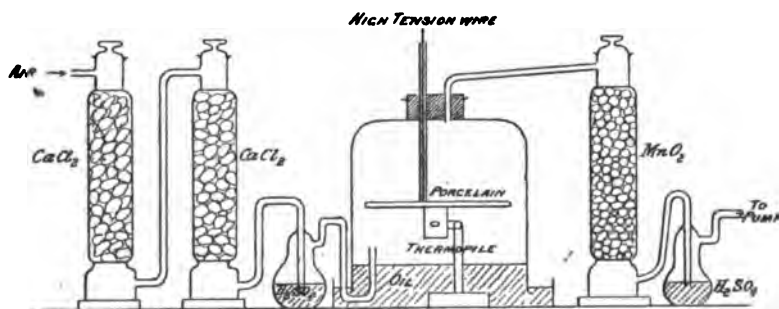
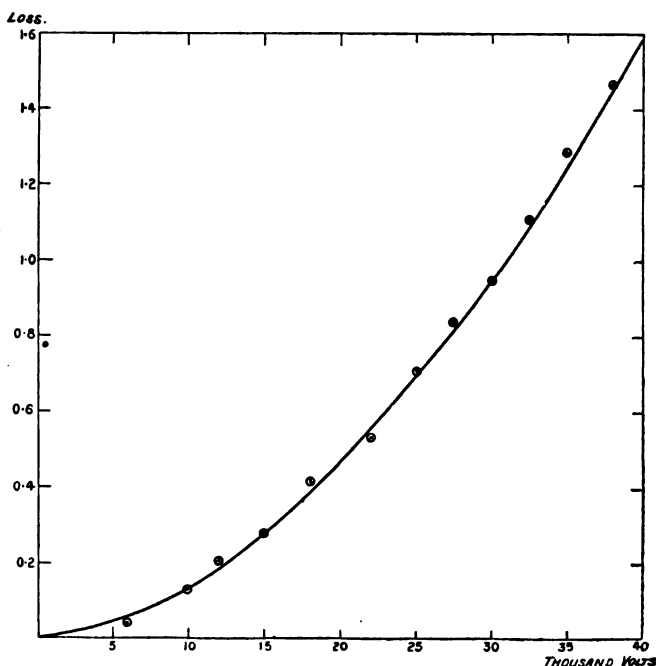


Diagram of Apparatus.

The dielectric loss was measured by the difference of temperature which could be maintained by the centre of the surface of the porcelain plate above atmospheric temperature. This temperature difference being only a

few degrees, it follows from Newton's laws of cooling, that the heat lost is proportional to this difference; and as the heat lost is equal to the heat gained, if the temperature is constant, a thermopile placed with one end in contact with the porcelain will generate an E.M.F. which is directly proportional to the dielectric loss. This E.M.F. was measured by connecting the thermopile with a low resistance galvanometer through a reversing switch, and noting the direct and the reversed deflections to neutralise the effect of local E.M.F.'s, etc. The losses were first measured at a constant frequency of 50 per second, with pressures up to 38,000 volts (R.M.S.). The results are graphically represented in Curve 9. The equation to the curve is expressed by

Loss per cycle  $\propto kV_{\text{R.M.S.}}^{1.74} = 1.83 \times 10^{-12} V^{1.74}$  Joule per cubic centimetre, where  $V$  is the R.M.S. potential gradient per centimetre.



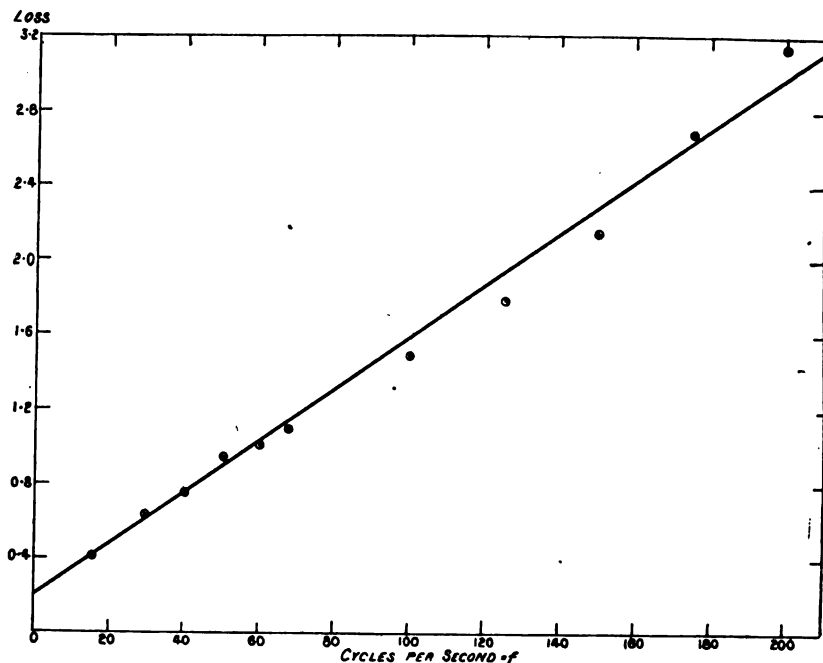
CURVE 9.—Potential-Loss Curve for Porcelain. Frequency Constant = 50.  
Loss  $\propto KV^{1.74}$ .

The losses were then determined at constant pressure (30,000 volts), and for frequencies between 15.8 and 200.

The points obtained lie practically on a straight line which does not pass through the origin (Curve 10), so we have the equation for the dielectric loss as follows:—

$$\left. \begin{array}{l} \text{Dielectric loss per cubic} \\ \text{centimetre in time } t \end{array} \right\} = 1.83 \times 10^{-12} V_{\text{R.M.S.}}^{1.74} (f + 14.4) t \text{ Joules,}$$

where  $V$  is the R.M.S. potential gradient per centimetre and  $f$  is the number of cycles per second.



CURVE 10.—Frequency-Loss Curve for Porcelain. Voltage Constant = 30,000 R.M.S.  
 $\text{Loss} \propto 0.0139 f + 0.2$ .  $K = 0.0000655$  mfd.

The constant 14.4 is probably due to the fact that porcelain is not a perfect insulator, and that a certain current would flow if a direct pressure of 30,000 volts was applied to it, giving rise to an ordinary  $C^2R$  loss.

We have here a striking similarity between magnetic and dielectric losses. They are each independent of the time in which the cycle is completed (if we neglect the  $C^2R$  loss due to the imperfection of the dielectric), and are proportional to similar powers of the amplitude of the cycle.

May we not extend this similarly to the internal actions? Let us imagine the dielectric to consist of electric instead of magnetic doublets: these particles would oscillate or revolve under the influence of an alternating electric field, and energy would be absorbed in overcoming their molecular friction.

#### *Dielectric Losses. Historical.*

In 1861, W. Siemens published a paper on the heating of the glass of a Leyden jar,\* and pointed out that a condenser became heated on charge and discharge. Many attempts have been made to measure the loss of energy in dielectrics subjected to a varying electric field.

\* 'Monatsber. d. Berlin Akad.,' October, 1861.

In 1890, J. Swinburne suggested\* that the loss was due to want of homogeneity in the dielectric, and imagined conducting channels to run across the dielectric, giving rise to a C<sup>2</sup>R loss. This view has been accepted by many subsequent investigators. In 1891, Major Cardew† attempted to measure the power factor of a paraffined paper condenser by the "Three Voltmeter" method, but the results obtained are doubtful.

In the same year Hutin and Leblanc,‡ working with paraffined paper condensers, also attributed the loss to heterogeneity of the dielectric, and came to the conclusion that they were dealing with the case studied by Poisson of a perfect dielectric, containing many small spheres of conducting material. They destroyed the fibre of the paper by strongly heating, and in doing so the dielectric constant fell from 8 to 2.56. The condenser then stood 1000 volts per centimetre without heating, but at higher pressures the temperature rose.

Steinmetz,§ experimenting on paraffined paper condensers, found the dielectric loss to vary as the square of the applied pressure. The pressures used varied between 80 and 320 volts at 170 ~; at higher pressures he found that the loss increased at a higher power than the square of the applied pressure. Steinmetz pointed out the analogy between the hysteresis loss in iron and dielectric loss, and so the name "Dielectric Hysteresis" was loosely given to any kind of dielectric loss.

Janet|| makes a similar remark, and says that solid dielectrics present phenomena quite analogous to magnetic hysteresis, in consequence of which, at equal pressures, the charge in a condenser is smaller for increasing than decreasing pressures.

Janet, in a later account,¶ experimenting on a mica condenser, obtained a curve enclosing an area for the relation between charge and P.D. analogous with a magnetic cycle in iron, but its form may be accounted for by hysteresis, or viscosity, or both.

By a hysteretic loss we mean one which is independent of the time taken for the cycle, and this point has been overlooked by many experimenters.

Hess\*\* agrees with Poisson in his case of a perfect dielectric containing conducting spheres, and deduces theoretically the existence of residual charge, and dielectric loss, and shows that the loss would agree with the results of

\* 'Phys. Soc. Proc.,' vol. 11, p. 49.

† 'I. E. E. Proc.,' May, 1891.

‡ 'La Lumière Électrique,' vol. 41, p. 179, July, 1891.

§ 'Electrical Engineer' of New York, March 16, 1892.

|| 'Comptes Rendus,' December, 1892.

¶ 'Comptes Rendus,' vol. 116, p. 373, February, 1893.

\*\* 'La Lumière Électrique,' vol. 46, p. 402, November, 1892.



Steinmetz and others. Hess does not think that the result obtained by Steinmetz,  $P = KE^2$  for dielectrics, can be considered as analogous to his law for magnetic hysteresis,  $P = KB^2$ , because, if dielectric hysteresis existed, it would be entirely swamped by the  $C^2R$  loss due to the conducting bodies.

Arnot\* suspended hollow cylinders of various substances in a rotating electric field, and showed that the cylinders had a tendency to turn; from this, Arnot calculated the energy expended in the dielectric, and called the loss hysteretic, although he might just as easily have attributed it to viscosity.

Bedell, Ballantyne and Williamson† employed a method similar to the one described on p. 234, and attributed the loss to hysteresis.

Porter and Morris‡ using very slow cycles of electrification, found the variation in charge of a condenser for equal pressures, on increasing or decreasing the potential, to be less than one in eight thousand, and so concluded that the effects were due to viscosity rather than hysteresis.

F. Beaulard§ found that the energy dissipated in different dielectrics at different frequencies varied with the time of the cycle, and tended to vanish as the time of the cycle increased. According to him, the loss was a viscous one.

E. E. Northrup|| shows that the value of the specific inductive capacity of a dielectric is larger for a slowly varying field than for a rapidly varying field.

Experiments of Blondlot and J. J. Thomson¶ show even greater changes.

H. Pellat\*\* tried to show that the energy loss was due to dielectric polarisation, and states†† that if a solid or liquid dielectric be suddenly placed in an electric field it polarises, the polarisation increasing with time, and tending to a maximum. If the field ceases, the polarisation diminishes to zero.

W. Schaufelberger‡‡ suspended ellipsoids of ebonite and paraffin bifilarly between the plates of a Kohlrausch condenser, and found the energy loss from the increased damping of the oscillations. In the case of paraffin the loss was proportional to the square of the field strength. Arnot found that they varied as the 1.8th-power of the field.

The following methods have also been adopted to determine the losses in dielectrics :—

\* 'Rendiconti R. Accad. Lincei,' October 16, 1892; 'The Electrician,' vol. 30, p. 516, March 3, 1893; 'La Lumière Électrique,' vol. 46, p. 536, December, 1892.

† 'Physical Review,' vol. 1, p. 81, October, 1893.

‡ 'Roy. Soc. Proc.,' vol. 54, p. 7, May, 1893; and vol. 57, p. 468, March, 1895.

§ 'Journ. de Physique,' August, 1900, pp. 422—437.

|| 'Phil. Mag.,' vol. 39, pp. 78 and 95, June, 1896.

¶ 'Recent Researches in Electricity and Magnetism,' p. 471, etc.

\*\* 'Annal. Chim. Phys.,' vol. 18, pp. 150—181, October, 1899.

†† 'Comptes Rendus,' vol. 128, pp. 1218—1220; also pp. 1312—1314, 1899.

‡‡ 'Wied. Ann.,' vol. 67, No. 2, pp. 307—324, 1892.

Kleiner\* used a thermo-couple embedded in the dielectric.

Bermischke† used a bolometer to determine the rise in temperature in a paraffin wax plate, but failed to detect any, and concluded that dielectric hysteresis did not exist. He attributed the losses to (1) Joule effect, (2) residual charges (viscosity), (3) mechanical losses due to vibration of condenser sheets.

Rowland and Penniman‡ used the split dynamometer method brought out by Professor Rowland; they experimented on paraffined paper condensers, and found the loss to increase with the frequency of the cycle. In other experiments they found that the loss per cycle was independent of the time of the cycle. These results are opposite to those of Porter and Morris, and it seems not unlikely that, under certain conditions, viscosity may be the predominating feature of the dielectric, and, under other conditions, hysteresis.

Rosa and Smith§ using a resonance method in conjunction with a wattmeter, found that the loss was proportional to the square of the current, and hence the loss might be attributed to the equivalent resistance of the condenser. The voltage varied from 400 to 2250, and the condenser was of paraffined paper.

Dr. P. Humman|| using the resonance wattmeter method with different kinds of cables, found that the loss was proportional to  $V^2 \sim$ .

#### *Summary.*

1. A porcelain condenser charges at a comparatively slow rate (Curve 1). This may account for the dielectric constant, as measured by alternating current, being smaller (7.18 at  $14^{\circ}3$  C.) than that measured by continuous current (8 at  $14^{\circ}3$  C.).

2. For pressures up to 1200 volts the charge was directly proportional to the pressure, if the potential changes were made slow enough (Curve 2).

3. If the potential changes were made rapidly, the charge was not quite proportional to the potential. There was a certain dielectric loss (Curve 3).

4. The dielectric constant, measured after one minute's electrification varied with the temperature according to the following laws:—

Between  $0^{\circ}$  and  $30^{\circ}$  C. ....  $C_t = C_0(1 + 0.00223t + 0.0005t^2)$ ,

Between  $30^{\circ}$  and  $100^{\circ}$  C. ....  $C_t = C_{100} \cdot e^{0.0064(t_1 - t_2)}$ .

The dielectric constant at  $20^{\circ}$  was 8.95 (Curve 4).

\* 'Wied. Ann.,' vol. 50, p. 138.

† 'Wiener Sitzber.,' No. 102, vol. 7, p. 1345.

‡ 'Phil. Mag.,' vol. 45, p. 66, 1898.

§ 'Phys. Review,' vol. 8, p. 4, January, 1899.

|| 'Inaug. Diss., Bonn, 1896, Extract, "El. Zeitschr.," 1898, pp. 435—436.

5. The apparent conductivity of porcelain varies with the applied pressure and the duration of the application. The dielectric polarises, or generates a back E.M.F., when a potential difference is applied to it (Curves 5 and 7).

The conducting mechanism shows viscosity.

6. The apparent conductivity of porcelain, measured after one minute's electrification, increases with the temperature according to the following law:—

$$\gamma_{t_1} = \gamma_{t_2} \cdot e^{0.090837 (t_1 - t_2)} \text{ (Curve 8).}$$

The specific conductivity at 20° C. is

$$0.2624 \times 10^{-13} \text{ mhos per centimetre cube.}$$

7. The dielectric loss varies as the 1.74th-power of the voltage (Curve 9), and is independent of the time of the cycle. The dielectric loss at high pressures and reasonable frequencies may be termed hysteretic. At very slow frequencies the loss is mainly C<sup>2</sup>R loss, and this shows viscosity effects; but these losses are swamped at working frequencies by the dielectric hysteresis (see Curve 10).

The dielectric constant is not affected by the electrostatic pressure, or by the frequency of the alternation of the electrostatic field, within the limits of the experiment.

The continuous current experiments of this research were carried out at the Physikalisches Institut des Eidgenössischen Polytechnikums, Zürich, and I have to thank Professor Dr. H. F. Weber for his valuable help. The alternating current experiments were carried out at the City and Guilds of London Central Technical College; and I am indebted to Professor W. E. Ayrton, F.R.S., and T. Mather, Esq., F.R.S., for the loan of apparatus and advice. Messrs. Kinnes, Parry, Lefebvre, and Northcote (students of the Central Technical College) assisted in the experimental work required for Table IV.

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*Note on a New Sounding Machine for use on Lakes and Rivers  
without a Boat.*

By E. J. GARWOOD, M.A., Sec. Geol. Soc.

(Communicated by Professor T. G. Bonney, F.R.S. Received May 15,—  
Read June 4, 1908.)

1. *Introduction.*

In the course of an investigation into the mode of origin of certain Alpine lakes in the Canton Ticino, it became obvious that no conclusive results could be arrived at so long as the subaqueous forms of these rock-basins remained unknown.

In the admirable detailed map published by the Swiss Government, no attempt has been made to represent by soundings the storage capacity of these Alpine reservoirs, a fact somewhat astonishing, at first sight, when we consider the great value of water power to the inhabitants of the Republic. The omission, however, becomes more intelligible when the difficulties involved in obtaining the necessary soundings are realised.

The majority of these lakes are situated in wild and uninhabited districts, where no boats are available, and though boats of the Berthon and Shellbend types have occasionally been employed in similar cases, their use is attended with many drawbacks, the chief of these being their instability and their liability to drift. The latter drawback renders them most unsuitable for work on mountain tarns where gusts and squalls are of constant occurrence.

Under these circumstances it seemed desirable, if possible, to devise an instrument which would enable an observer to obtain an accurate bathymetrical chart of any mountain lake without being dependent upon a boat.

With the assistance of a grant of £15 from the Government Grant Committee of this Society, which I here gratefully acknowledge, an experimental model was designed, which gave satisfactory results. The knowledge thus acquired was made use of in the construction of a second, more efficient instrument, with which a group of lakes in the Canton Ticino was successfully charted. The results of the investigation were published in the 'Quarterly Journal of the Geological Society' (vol. 62, 1906, p. 165, Plates 7—21).

The instrument, which is here described for the first time, is the outcome of the experience thus gained, and in it are embodied alterations and additions suggested by practical experience acquired in working with the two previous models. Its chief advantages are:—

- (1) Its portability. It can easily be carried by one man even in mountain districts.
- (2) It can be used where no boats are available.
- (3) It is practically unaffected by any ordinary breeze, so that a line of soundings may be run between any two points in a nearly straight line from shore to shore.
- (4) Not only the depth of each sounding but the distance from the shore at which it is taken is automatically registered.

### *2. General Description of the Instrument.*

The instrument consists essentially of two posts (A and B) erected on opposite sides of the lake or river, manipulated respectively by the observer and his assistant, who work gradually down from one end of the lake to the other. The posts are connected by a line, to the centre of which is attached a float carrying a pulley for the support of the plummet line. The ends of the connecting line are wound on two drums (Y and Z) fitted to the posts A and B. By means of these drums the float can be drawn backwards and forwards across the lake, and thus takes the place of a boat in the usual method of sounding.

The post B, in charge of the assistant, carries nothing but this drum (Z, fig. 2), fitted with a stop-brake, and the duty of the assistant is merely to haul in and let out the float as directed. This is an important point in the construction of the machine, as it enables any boy or untrained assistant to be utilised for the purpose, all registering mechanism being confined to the post A.

The post A (fig. 1) is worked by the observer. It is provided with two drums (X and Y) accurately paired and placed on either side of the post. These are fitted to an axle which is common to both. The drum Y is firmly fixed to this axle and always revolves with it; the drum X can also be arranged so as to revolve *with* the axle by dropping the spring bolt (*a*), it then revolves with the drum Y; by raising the bolt (*a*), however, the drum X is set free and can revolve independently *on* the axle.

The line from the drum Y, as stated above, is attached to one end of the float, while the line from the drum X is the sounding line and travels through a counting machine W to the centre of the float, where it passes over the pulley to the plummet. The drum X is fitted with a check (*b*), worked by a lever on the right-hand edge of the post.\* This prevents the drum from racing when the plummet is running out, and can also be brought into action for the same purpose when the wheels are coupled and the float is being drawn to a new position.

\* Right and left hand from the point of view of an observer facing the counting machine.

## GARWOOD SOUNDING MACHINE.

**SCALE 1:6.5.**

— FIG. 1 —

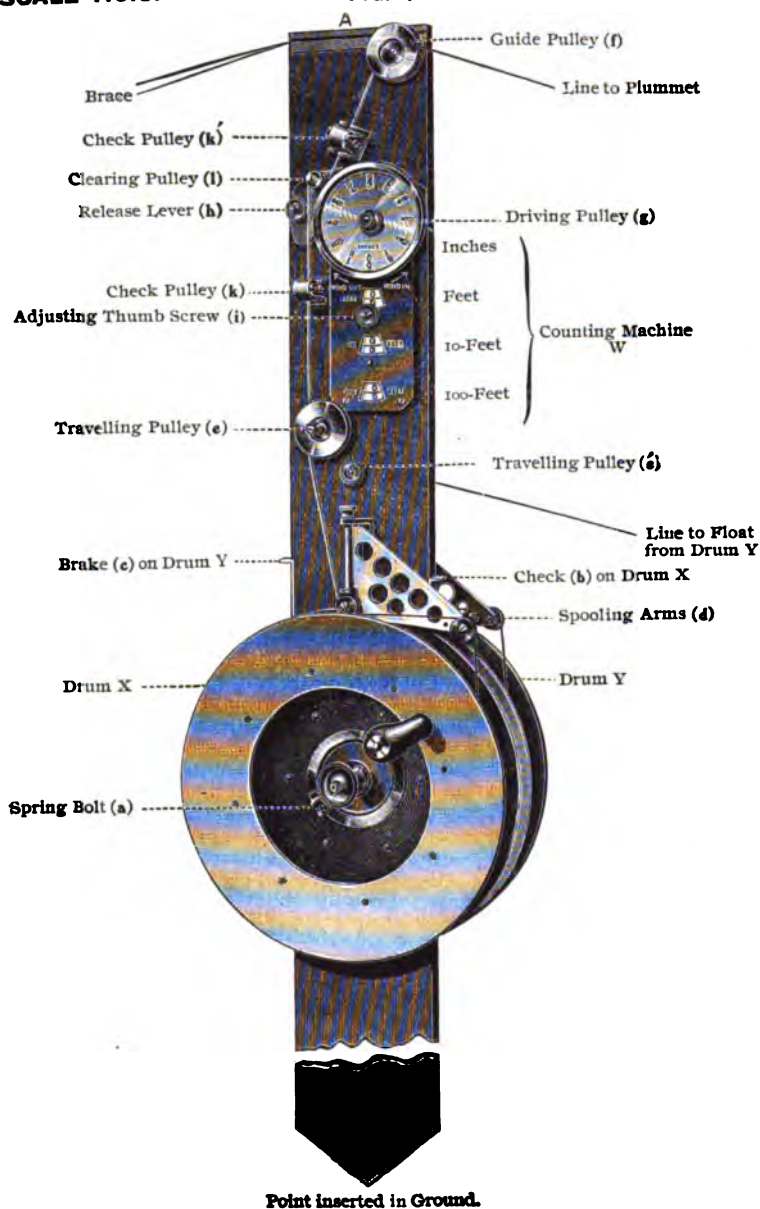


FIG. 1.

The drum Y is fitted with a stop-brake worked by a sliding lever (*c*) on the left-hand edge of the post.\* This brake works on the toothed edge of a plate fixed to the inner side of the drum, and brings this drum instantaneously to rest. By dropping the bolt (*a*) and thus coupling X and Y, the drum X is also rendered stationary when this brake is applied.

The two lines are fed on to the drums by means of the spooling arms (*d*), which are coupled and move together horizontally across the faces of the drums. These spooling arms are supplied to prevent the lines from piling. Should, however, piling take place, it will be forced to do so symmetrically on both drums, and the lines are thus kept equally taut. Without this device the plummet is liable to drag behind and become caught in shallow water. The free movement of the spooling arms is ensured by the travelling pulleys (*e*, *e'*). The line from the drum Y travels from the pulley *e'* to the float.

The sounding line from drum X, after leaving the travelling pulley (*e*), passes through the counting machine W and over the guide pulley (*f*) to the plummet.

*The Counting Machine W* is driven by the plummet line, which passes round the large pulley (*g*), forming the first counting disc and registering inches. Three other counting discs, geared to (*g*), register feet, tens of feet, and hundreds of feet respectively. Each of the discs is engraved with a double series of numbers in red and black, registering in opposite directions, by means of which the machine can be made to record either the amount of line let out or the amount drawn in.

By loosening a thumb-screw, the lever (*h*) can be raised and the driving pulley (*g*) and the sounding line disengaged from the remaining portion of the counting machine. The dials, recording feet, can then be rapidly returned to zero by the adjusting thumb-screw (*i*), the plummet line meantime remaining at rest. The constant tension of the line on the driving pulley is secured by means of the spring roller clips (*k*, *k'*), while the line is prevented from running off the side of the driving pulley by the clearing pulley (*l*), which ensures the line crossing freely, clear of the machine.

*The Float* consists of an inflated air cushion of lifebuoy pattern. This supports an aluminium platform, the centre of which is perforated for the passage of the plummet line, which runs over a pulley fixed to the platform at the margin of the perforation (fig. 2). When the lake is wide, it is sometimes convenient to add a small supplementary float to support the lines and to prevent them from sinking too far under water.

\* Right and left hand from the point of view of an observer facing the counting machine.

*The Line* actually used is a plaited waterproofed salmon line.\* Stronger line or fine wire can be used for distances and depths greater than those usually met with in small Alpine lakes or ordinary rivers.

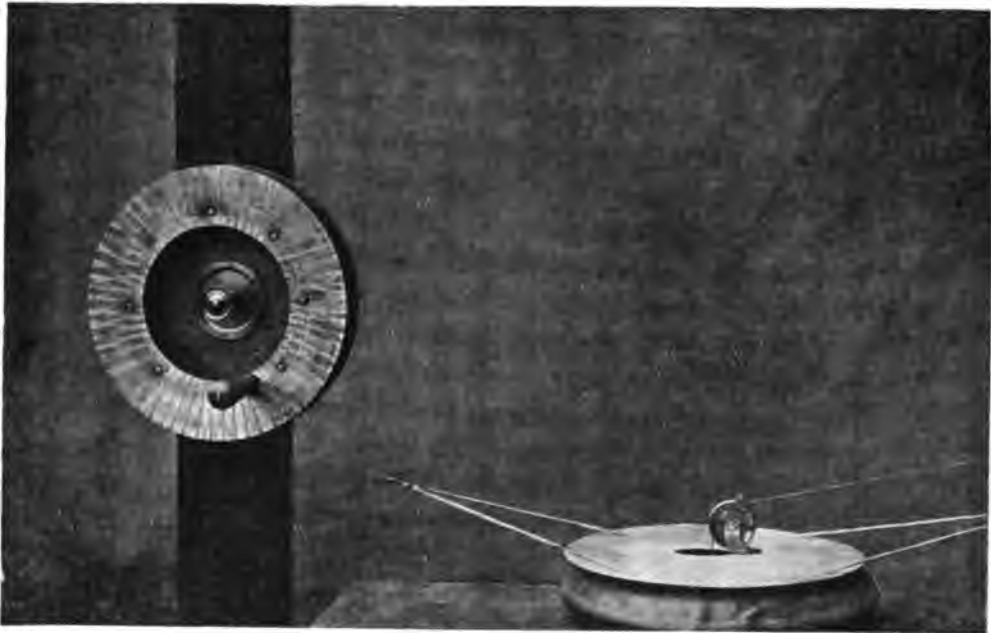


FIG. 2.—Showing Post B, Drum Z, and Float carrying Sounding Line.

### 3. *Method of using the Instrument.*

Starting with his assistant near one end of the lake, the observer erects the post A in a position suitable for taking a line of soundings across the lake. The assistant proceeds to a selected spot on the opposite shore, where he erects the post B, leaving with the observer the float, to which the end of his line is attached. He then winds this line taut, thus establishing direct communication between the opposite shores of the lake. The float can now be hauled across the lake and a line of soundings obtained at intervals between the two posts (fig. 3).

The two drums X and Y on the observer's post being coupled by means of the spring bolt (*a*), and the counting machine being at zero, the assistant winds in his line until a given distance, say 25 feet, is registered by the *red* figures on the counting machine. This records the distance that the float has travelled out from the observer's shore. The lever of the brake *c* is then raised, locking both drums securely. The spring bolt (*a*) is next drawn from

\* Supplied by Messrs. Carter and Co., St. John Street, London, E.C.





When the first line of soundings is completed and the float has reached the post B, the observer or his assistant moves further down the lake. The counting machine having been returned to zero, the observer proceeds to haul back the float to his side of the lake, taking soundings at intervals as before. The *black*, not the *red*, figures are now used.

It must be remembered, however, in the case of this second series of soundings, that, since the plummet line as well as the float line is being hauled in by the observer, the figure representing the depth of the lake, at any sounding, will be *deducted* on the dial from the figure representing the distance from the shore for the position of that sounding; for the plummet line, in running out, will move the registering dial in the opposite direction to that in which it is moved when the float is being hauled towards the observer. Thus:—

Amount registered by <i>black</i> figures representing distance from	
shore when plummet is at surface .....	25 ft.
Ditto when plummet is at bottom.....	5 „
∴ Depth of lake at 25 ft. from <i>assistant's</i> shore is (25—5 ft.) = 20 ft.	

The red figures can, of course, be used for taking the sounding if their position is noted each time. In practice, however, it is found to be more convenient to proceed as stated above.

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*The Viscosity of Ice.*

By R. M. DEELEY, F.G.S.

(Communicated by Henry Woodward, LL.D., F.R.S., F.G.S. Received May 18,—  
Read June 4, 1908.)

Although the character of the motion of glaciers is now well known, and the velocity of their motion has, in some cases, been measured, calculations do not appear to have been made of the viscosity of either glacier or crystalline ice; nor do there appear to be any published figures from which the viscosity can be quite accurately ascertained. It is possible, however, by estimating certain dimensions, to obtain results which, although not strictly accurate, give figures of the proper order of magnitude.

The property termed viscosity is here used as defined by Maxwell.\* A tallow candle is much softer than a stick of sealing-wax; but, if the candle and the stick of sealing-wax are laid horizontally between two supports, the sealing-wax will, in a few weeks in summer, bend with its own weight, while the candle remains straight. The candle is, therefore, a soft solid, and the sealing-wax a very viscous liquid. A viscous body is considered as one which undergoes permanent and continuous change of form under the action of a stress, however small. A plastic body is one which requires a definite and often increasing stress to produce continuous change of form. For all practical purposes, a substance which undergoes continuous change of form under very small stresses and yields at a rate proportional to the stress may be regarded as viscous. I have previously given some formulæ† for calculating the viscosity of liquids, but did not then apply them to any concrete case. This I now propose attempting.

If a bed of a glacier were fairly symmetrical and the ice obeyed the laws of viscous flow, then the ice would move faster in the middle and more slowly at the sides and bottom. The rate of flow was carefully measured by Tyndall, who placed a straight line of stakes across a glacier and found that in the course of a few hours the straight line became bent into a curve. We have no measurements which show that this curve is strictly parabolic in the case of any particular glacier, nor can we expect to find such, for the valleys down which glaciers move are generally sinuous and have irregularities in their beds.

Above Trélaporte, on the Mer de Glace, crevasses form right across the ice, and into these crevasses the rock debris on the glacier falls. When, by

\* 'Theory of Heat,' 1894 edition, p. 303.

† 'Geol. Mag.,' September, 1895, p. 408.

melting of the ice surface, these dirt bands become visible lower down, the dirt bands are seen to stretch across the glacier in great parabolic curves.

The downward movement of a glacier is due to its weight and viscosity. In the case of a fluid of small viscosity, such as water, inertia effects cause the stream to be swifter in some places than can be due to the slope there, and slower at other places. With a glacier, the viscosity of which is enormous, the great viscosity enables it to transmit thrust to some considerable distance, and for this reason we get velocities at various points which are not wholly due to the effects of gravity at such points. The surface melting of glaciers also causes them to undergo longitudinal compression in many cases, and this again complicates the question.

Tyndall measured the rate of flow of a number of glaciers, the slopes of the upper surfaces of which can be approximately obtained. Their thicknesses, however, can only be estimated. This I have done by comparing the valleys down which the glaciers move with other valleys of somewhat similar width and length. I consider it probable that the slip at the bottom is about 15 per cent. of the surface velocity, so that the effective difference of velocity between top and bottom is 75 per cent. of the surface velocity. The rock being dense and hard, the probability of the glacier being frozen to its bed does not seem great. The breadth of the glaciers being much in excess of their thicknesses, and it being probable that the slip is much greater at the sides than at the bottom, the assumption has been made in the calculations that the glaciers are of infinite width.

In Table I are given both the calculated viscosities for a number of glaciers and the figures upon which the calculations are based. These figures will be subjected to criticism and modified if more accurate estimates of the data can be made.

As an instance of the method adopted, the calculation for obtaining viscosity of the Great Aletsch glacier is given below :—

$$\begin{aligned} P &= \text{bodily force producing motion, being downward component of gravity} \\ &= \text{gravity} \times \text{density} \times \text{gradient} \\ &= 980.5 \times 0.92 \times 65/1000 = 58.634 \text{ dynes per cubic centimetre.} \end{aligned}$$

By observation, the maximum velocity  $V$  is 0.00047 cm. per sec. and the depth  $r$  is at the bottom of the glacier 45,000 cm.

The equation of flow,  $\frac{d}{dr} \left( \mu \frac{dv}{dr} \right) = P$ , leads to

$$\mu \frac{dv}{dr} = Pr, \text{ and } \mu = \frac{Pr^2}{2V} = \frac{58.634 \times 45,000^2}{2 \times 0.00047} = 126,224,200,000,000,$$

say  $126 \times 10^{12}$ , the viscosity of water being only 0.01028 at 20° C.

The maximum shearing stress at the bottom of the glacier tending to drag the rocky surface along with it is the total downward component of gravity,

$$Pr = 3.731 \times 1476.4 = 5510 \text{ lbs. per sq. ft.}$$

In many cases glaciers have in my opinion\* been frozen to their beds, and have dragged along with them, and crumpled and contorted, the rocks over which they have passed.

The shear at the bottom of the Great Aletsch glacier, amounting to nearly  $2\frac{1}{2}$  tons per square foot, is the average near the centre. This figure may be greatly exceeded at points where a rock projects above the general surface; for owing to the very great viscosity of the ice, thrust can be transmitted very considerable distances.

Although glacier grains are capable of being deformed easily by a stress producing shear at right angles to the optic axis, yet from the fact that these grains have their axes at all angles, the motion of the glacier must be partly due to some other assisting cause. This I have suggested is the liquefaction and regelation† which takes place when molecules pass from crystal to crystal.‡ An ice crystal may evaporate more freely on one face than another, thus causing a permanent and continuous transfer of molecules from crystal to crystal. McConnel states that a bar of ice with which he experimented decreased in width when the optic axis was vertical more rapidly than it decreased in depth.

The effective viscosities of glaciers referred to in Table I range according to these calculations from  $292.2 \times 10^{12}$  to  $3.27 \times 10^{12}$ . It is admitted that the data are somewhat uncertain; but as far as rate of movement, slope, and thickness are concerned, the errors can scarcely be as great as will account for the whole of this difference. The most serious uncertainties are the extent to which thrust and the amount of slip at the boundaries may affect the results. In the case of the Great Aletsch the regularity of the slope and the great length of the ice stream seem to show that there is no rock basin of any depth below the stream, and the value of the viscosity obtained for it is probably the most reliable. Both the Mer de Glace and the Lower Grindelwald glaciers are in compression and the smaller values may be partly due to this, *i.e.* to thrust giving a more rapid motion than is due to the slope only. In these two ice streams the glacier grains may also be smaller, owing to the nearness of the *néve* and the presence of ice falls, and this may cause the viscosity to be small.

The Morteratsch results are also likely to be affected by thrust, especially

\* 'Geol. Mag.,' 1897, p. 394.

† 'Phil. Mag.,' February, 1888.

‡ 'Geol. Mag.,' May, 1895, p. 161; 'Phil. Mag.,' May, 1895.

towards the end, and a mean of the three viscosities obtained for this glacier may be considered to be fairly free from error.

Table I.—Viscosity of Glacier Ice.

Glacier.	Thickness, metres.	Velocity.		Slope.	Pressure in dynes per cm. <sup>2</sup>	Viscosity $\mu$ , in c.g.s. units.
		Including slip.	Without slip.			
		Inches per day.	Inches per day.	One in		
Mer de Glace—						
At Trélaporte .....	210	20	17	13·5	66·82	$29·48 \times 10^{12}$
At les Ponts .....	210	23	20½	12	75·17	27·51
Above Montanvert...	210	26	22½	11	82·00	27·64
At Montanvert .....	210	34	29	10	90·20	23·33
Below Montanvert...	210	33	28	10	90·20	24·16
Morteratsch, Pontre-						
sina—						
High up .....	400	14	12	7	128·90	292·2
Middle.....	290	11	9	10	90·20	143·4
Above end .....	190	7	6	10	90·20	92·31
Lower Grindelwald ...	100	22	18½	25	36·09	3·274
Great Aletsch.....	450	—	16	15·4	58·63	126·2

A viscosity of  $125 \times 10^{12}$  appears to be as near an estimate as can yet be made of the average effective viscosity of a Swiss glacier. In winter the viscosity is probably double this figure owing to the lower temperature.

J. C. McConnell\* appears to have been the first to observe the exact conditions under which ice is capable of being deformed without fracture by stress. He showed that a crystal of ice can be sheared by very small stresses in a direction at right angles to the optic axis, and that the rate of shear becomes greater as the stress is increased. His two main conclusions are (1) that the friction between the particles of ice along the shear planes becomes greater as the temperature falls, (2) that when the molecules of ice slide over each other the cube of the friction varies as the square of the velocity. It must be remembered that McConnell died before his paper was quite finished, and that, therefore, his calculations were not completed, nor was his paper subjected to final correction. It will, consequently, not be out of place to reconsider his experimental results in detail.

In Table II, I have set out a number of the experimental results he

\* 'Roy. Soc. Proc.,' May, 1891, p. 323.

obtained with bars of ice loaded with various weights. Although in one place only he states the distance between the supports of the ice bars, it is clear that the distance was 51 mm. He used a solid iron frame placed in a small box to keep the temperature from varying rapidly, and to check evaporation. In no case is the full length of the ice bar given; this I have assumed to be 60 mm. He states that during the experiments the bars lost weight by evaporation, and as he gives the rate of evaporation, I have calculated the probable size of the bar at each reading of deflection. This can readily be done, as McConnel gives the size of the bar before and at the end of the experiment, and also gives the times when the weights were altered and the deflections were measured. In a few cases the figures he gives for the duration of the tests are slightly in error; these have been corrected.

Table II.—Experiments made by J. C. McConnel.\*

Time, hours.	Bending, mm.	Weight, kilos.	Breadth, mm.	Depth, mm.	Temp., ° C.	Shear F., dynes per cm. <sup>2</sup>	Viscosity, c.g.s. units.
0·5000	0·118	2·5	14·61	12·27	— 6·7	68·5 × 10 <sup>4</sup>	22·64 × 10 <sup>10</sup>
0·5167	0·069	2·5	14·59	12·26	— 7·2	68·6	31·07
1·167	0·066	1·445	14·57	12·24	— 6·7	39·8	42·17
1·167	0·128	1·445	14·53	12·22	— 6·7	40·0	28·45
1·867	0·125	0·915	14·44	12·16	— 8·9	25·7	29·90
1·483	0·066	0·915	14·37	12·12	— 10·0	25·9	34·81
14·83	0·066	0·295	14·10	11·93	— 15·0	8·7	117·20
0·8	0·328	2·5	13·84	11·76	— 8·9	75·4	14·35
0·7	0·032	2·5	11·56	13·50	— 15·3	78·6	134·20
2·333	0·272	2·5	11·51	13·47	— 11·1	79·2	52·99
0·6833	0·260	2·5	11·45	13·44	— 7·0	79·7	16·35
0·2667	0·167	2·5	11·44	13·43	— 5·6	79·9	10·59
0·275	0·257	2·5	11·43	13·42	— 3·9	80·0	6·68
0·1916	0·257	2·5	11·42	13·41	— 2·8	80·1	4·66
0·1083	0·164	2·5	11·42	13·41	— 2·2	80·1	4·13
0·1083	0·204	2·5	11·41	13·41	— 1·7	80·2	3·32
0·2416	0·310	2·5	11·38	13·39	— 6·1	80·5	4·90
0·4083	0·304	2·5	11·23	13·29	— 13·0	82·2	8·62
0·6416	0·440	2·5	11·21	13·27	— 13·2	82·5	9·39
3·917	0·146	2·5	16·03	17·73	— 5·0	43·2	90·50
1·408	0·227	2·5	15·95	17·67	— 5·0	43·6	21·10
1·542	0·084	1·29	15·90	17·63	— 6·7	22·7	32·47
0·4583	0·073	2·5	15·86	17·61	— 7·5	44·0	21·55
0·4	0·119	3·79	15·84	17·60	— 8·0	66·8	17·51
1·058	0·342	3·79	15·82	17·58	— 8·9	66·9	16·15
0·7416	0·146	2·5	15·79	17·56	— 10·0	44·3	17·56
12·63	0·288	0·62	15·56	17·41	— 7·8	11·3	39·39
0·5916	0·165	2·5	15·33	17·26	— 6·1	46·4	12·99
0·4083	0·235	3·79	15·31	17·24	— 5·9	70·5	9·56

\* See 'Roy. Soc. Proc.,' March 12, 1891, p. 323.

Fig. 1 shows a bent bar of ice resting upon its supports with the optic axis vertical. When the bar is bent the ice assumes the form given by the dotted lines at the point of flexure; but for all practical purposes it may be

assumed that the bending is as shown by the full lines. This assumption much simplifies the calculations, and does not appear to me to introduce any serious error.

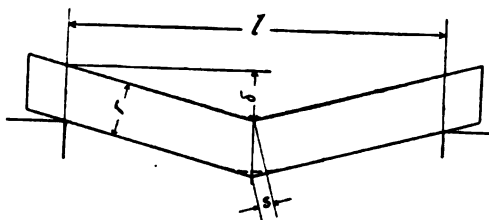


FIG. 1.

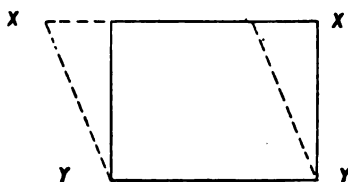


FIG. 2.

When, as shown in fig. 2, a mass of a viscous substance is distorted by the application of a stress to the plane XX, and the plane YY is fixed, the distortion is as shown by the dotted lines, and the stress at all planes between and parallel to the planes XX and YY is the same. Now, according to fig. 1, the ice bar is distorted by shear in exactly the same way, and I have regarded the weight on the centre of the bar as producing a stress parallel with and coincident with the upper and lower faces of the bar.

#### Calculations for Viscosity.

$l$  = distance between supports, centimetres.

$\delta$  = deflection, centimetres.

$r$  = thickness, centimetres.

$A$  = total area of horizontal surface, square centimetres.

$h$  = time, hours.

$W$  = load, dynes.

The shear  $\sigma$  is  $\delta/\frac{1}{2}lh$  per hour; the total shearing force in the cross-section is  $\mu A' \sigma / 60^2$ , where  $A'$  is the area of the cross-section. This must be equal to  $\frac{1}{2}W$ , so that

$$\mu = \frac{900Wh}{A'\delta}.$$

For the ninth test of Table II,

$$l = 5.1; \delta = 0.0032; r = 1.35; A' = 1.35 \times 1.156; h = 0.7;$$

$$W = 2500 \times 981 = 2,452,500,$$

so that

$$\mu = 134.2 \times 10^{10},$$

$$\text{and the shearing force} = \frac{W}{2A'} = \frac{2,452,500}{2 \times 1.561} = 78.6 \times 10^4.$$

In the last two columns of Table II are given the shearing stresses to which the bars were subjected and also the viscosities.



On Diagram I these viscosities are plotted, and against each plotting is marked the shearing stress (in dynes per square centimetre  $\times 10^4$ ) to which the ice was subjected.

The equation to the curve on the diagram is

$$\log_{10} \mu = 0.301 + 0.153t - 0.00231t^2,$$

so that  $\log \mu$  is parabolic, where  $\mu$  is the viscosity in dynes per square centimetre  $\times 10^{10}$  and  $t$  is the temperature below zero C (considered positive).

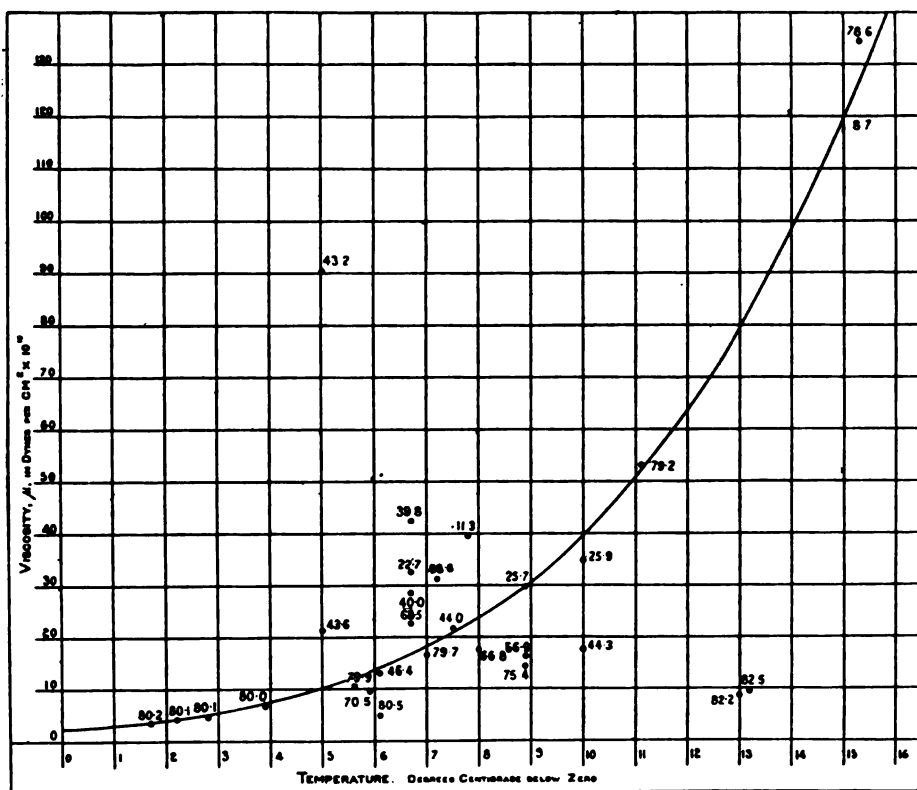


DIAGRAM I.

It will be noticed that out of 29 tests, one of which is stated by McConnel to be inaccurate, and two more of which also appear unreliable, leaving 26 presumably accurate results, 14, or more than half, give results agreeing within 5 units with the curve. The want of exact agreement with the curve seems to be mainly due to the varying temperatures experienced during the continuance of the experiments.

McConnel's experiments show that when the weight was taken off the ice-bar, in addition to purely elastic rise it recovered slowly some of the bending

the weight had produced. Many, if not all, soft solids do this. The recovery was very slow, and almost ceased after a time.

It will be seen, on referring to Diagram I, that the experiments made with the small stresses give, in some slight degree, the greatest viscosities, but this is not true to anything like the extent McConnel thought. In this connection he states that when the weight is changed the alteration in the rate of depression is great out of all proportion, *e.g.*, the alteration in the rate of bending from 0.0058 to 0.41 when the weight is changed from 0.295 to 2.5 kilos. In this case, however, there was a change of temperature from  $-15^{\circ}$  C. to  $-8^{\circ}.9$ , and, as will be seen from the diagram, the change of temperature will account for almost the whole of the change of viscosity. He should have compared the case in which the temperature was  $-15^{\circ}$  with the one in which it was  $-15^{\circ}.3$  C., and he would have found that, with stress varying in the proportion of 1 to 9, the rate of shear was very nearly proportional to the stress.

Mugg found that continuous shear could not be produced in some samples of ice when very lightly stressed.

It may be that the small departure from the rate of shear being proportional to the stress, when the stress is small, is to some extent due to want of regularity in the structure of the ice tested, and may also be in some measure connected with the property ice possesses of slightly recovering its original form after distortion.

There being some uncertainty as to the actual behaviour of other highly viscous substances under stress, I made some experiments with a bar of pitch. It was shaped by heating and pressing into a bar 150 mm. long and 14 mm. square, and placed upon supports 117 mm. apart. The load at the centre of the bar was 98.5 grammes, partly due to the weight of the bar itself and the finger used to indicate the bending. After the application of the weight, the bar was allowed to bend until the finger reached the scale. The readings then taken are given in Table III. At 12.19 P.M. a weight of 67.6 grammes was removed from the centre of the bar, which was then stressed only by the finger resting upon it and its own weight. After the removal of the weight, readings were taken for a time every 15 seconds. On Diagram II some of the readings taken before and after the weight was removed are plotted. The diagram shows that there was an elastic unbending of the bar, followed by a further slow unbending, which ceased in about 4 minutes. The bar then again began to yield viscously under its own weight.

From this it is concluded that a viscous substance under stress requires time after a change in the magnitude of the stress has been made for the rate of shear to become proportional to the altered stress. Also, that a

viscous (liquid) substance may be elastic, brittle, and may be able to partly regain its shape after being deformed by viscous distortion.

Table III.—Sample of Pitch. April 17, 1908. Bar 150 mm. long, 14 mm. broad, 14 mm. deep. Supports 117 mm. apart.

Time.	Deflection, mm.	Weight.	Temperature, ° C.
11.30	0.50	On	12.8
11.47	1.00	"	12.8
12.1	1.37	"	12.9
12.10½	1.62	"	12.9
12.19	1.87	"	12.95
12.19½	1.77	Off	12.95
12.20	1.75	"	12.95
12.20½	1.73	"	12.95
12.20¾	1.71	"	12.95
12.23	1.69	"	12.95
12.31	1.70	"	13.0
12.56	1.71	"	12.95
1.53	1.75	"	12.75
3.11	1.92	"	12.8

During the experiment with pitch, the thermometer and experimental apparatus were protected by a glass case and duster.

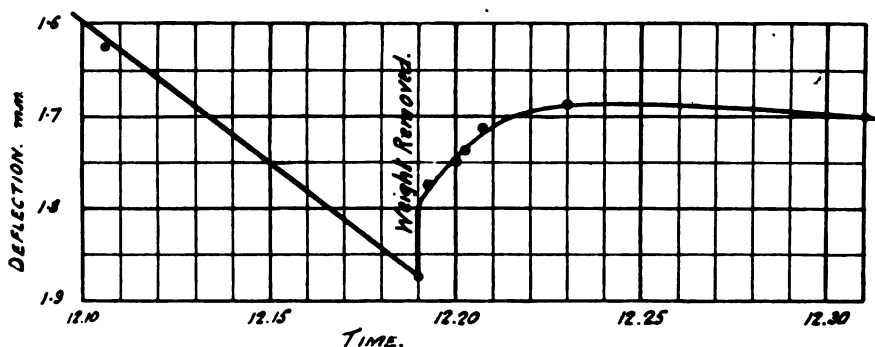


DIAGRAM II.

Since writing the above, my attention has been called to the experiments made by Trouton\* on several viscous substances, including pitch. He states that "it was noticed that there was a slow partial movement towards recovery on removal of the force of traction, which gradually fell to zero with time."

We may, I think, fairly conclude, from a consideration of McConnel's experiments and these above described on pitch, that the nature of the shear

\* 'Roy. Soc. Proc.,' vol. 77, p. 429.

which can be produced in an ice-crystal at right angles to the optic axis very closely obeys the laws of viscous flow. If this view should be sustained, it is not only true, as Professor H. A. Miers shows, that a liquid of low viscosity may have a crystalline structure, but also that, as in the case of crystalline ice, a solid may be liquid along one plane only.

From the equation to the curve on Diagram I, the viscosity of an ice-crystal in a direction at right angles to the optic axis is about  $2 \times 10^{10}$  at the freezing point. At this temperature the viscosity of a glacier is about  $12,500 \times 10^{10}$ , or 6250 times as great. The effective viscosity of a glacier is therefore due in a great measure to some other consideration. The optic axes of glacier grains are at all angles and they lock each other.

I am much indebted to Mr. P. H. Parr for the assistance he has rendered in calculating the results from the figures given.

*Vortices in Oscillating Liquid.*

By LORD RAYLEIGH, O.M., Pres. R.S.

(Received July 25, 1908.)

In a paper "on the Circulation of Air observed in Kundt's Tubes, and on some Allied Acoustical Problems,"\* I applied the equations of viscous incompressible fluid to show that the effect of the bottom of the containing vessel was to generate permanent vortices in the vibrating fluid. It was remarkable that the intensity of the vortical motion, when fully established, proved to be independent of the magnitude of the viscosity, so that the effects could not be eliminated by merely supposing the viscosity to become extremely small. The expression found for the vortices was simple. The horizontal component  $u$  of the primary motion near the bottom being  $u = u_0 \cos kx \cos nt$ , the component velocities of the vortical motion are

$$u' = \frac{2}{3} \frac{u_0^2 \sin 2kx}{V} e^{-2ky} (1 - 2ky),$$

$$-v' = \frac{2}{3} \frac{u_0^2 \cos 2kx}{V} e^{-2ky} 2ky,$$

$y$  being measured upwards from the bottom, and  $V (= n/k)$  the velocity of propagation of waves of the length in question. According to these

\* 'Phil. Trans.,' vol. 175, p. 1, 1883; 'Scientific Papers,' vol. 2, p. 239.

expressions, the vortical motion is downwards over the places where  $u$  has its greatest alternating values. In the case of water contained in a tank and vibrating in its simplest mode, the theoretical motion is downwards in the middle and upwards at the ends. To guard against misinterpretation, it may be well to add that quite close to the bottom the motion, as calculated, is of a quite different character.

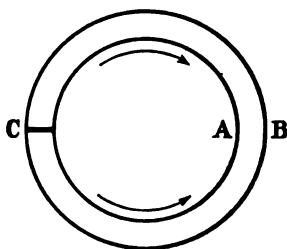
In a recent paper,\* Mrs. Ayrton has examined, with much experimental skill, the vortices arising when water oscillates in a narrow tank, and has obtained results which differ somewhat widely from what are indicated in the above formulæ. Near the bottom, and especially when the depth is small, there are indeed vortices of this character; but, in general, the most conspicuous feature consists of vortices revolving in the opposite direction, the water rising in the middle of the tank and falling at the ends. The first thought that occurred to me was that Mrs. Ayrton's vortices might be due to defect of freedom in the surface, such as might be supposed to arise from a greasy film opposing extensions and contractions; but in some experiments that I tried, the vortical motion did not seem to be much influenced by cleansing the surface, and the question was suggested as to whether the free surface itself might not originate vortices in somewhat the same way as the bottom does, and more potently on account of the greater velocities of the primary motion there prevailing. I do not remember whether I had any clear view on this question when I wrote the former paper. Vortices originating otherwise than at the bottom were ignored, but I may not have intended to exclude their possibility.

The present paper consists mainly of an attempt to answer the question thus suggested. The investigation is limited to the case of deep water, and even then is rather complicated. If the calculations are correct, we are to conclude that a free surface does *not* generate vortices of this kind, at least if we suppose the viscosity small and include only the square of the motion. How then are the conspicuous vortices, observed by Mrs. Ayrton, to be explained? One might attribute them to the ends of the tank, acting much as the bottom does in my former investigation. In the latter case the seat of the forces is near the parts lying midway between the middle of the tank and the ends ( $kx = \pm \frac{1}{2}\pi$ ), and their effect is to push the neighbouring fluid in the direction away from the place of greatest motion ( $kx = 0$ ). A like action at the ends of the tank would push the neighbouring fluid downwards, and thus generate vortices revolving in the observed direction. An objection to this view lies in an observation by Mrs. Ayrton on water oscillating in a long

\* "On the Non-Periodic or Residual Motion of Water moving in Stationary Waves," 'Roy. Soc. Proc.,' A, vol. 80, p. 252, 1908.

tank with several subdivisions (p. 255). Since no solid walls are situated at the intermediate nodes, it may be thought that the action at the ends would be insufficient to establish the whole system of vortices. Probably this would be so. But another influence acting in the same direction may arise from the *faces* of the somewhat narrow tanks employed. It would seem that at the nodes,  $kx = \pm \frac{1}{2} (2m+1) \pi$ , the friction in moving up and down along the faces might have the same general effect as the up-and-down motion along the solid walls which constitute the ends.

But I must confess that some observations made with the help of Mrs. Sidgwick were not favourable to this view. The ends of the tank were eliminated by using the annular space included between two coaxial cylinders, A, B (beakers), but the vortical motion did not seem to be diminished. The insertion of a strip of glass C held vertically across the annulus, and thus virtually restoring one end, did not make much, if any,



difference. This experiment seems to exclude the explanation depending upon the action of the *ends*, and that which would attribute the effect to the *faces* is difficult to reconcile with the highly localised character of the effect, which at first seems to be limited to the immediate neighbourhood of the ends. Can it be that the true explanation would require the retention of terms of higher order than the *square* of the motion?

I may mention that on more than one occasion I have witnessed the reversed movement described by Mrs. Ayrton on p. 259, "as if a set of water springs had been wound up, and now proceeded to unwind themselves." I presume that the spring depends upon gravity, acting upon unequal densities in the fluid, due either to temperature or to variations in the amount of powder held in suspension. Another possible explanation would lie in the effect of surface contamination.

In the usual notation the equations of motion in two dimensions are

$$\frac{1}{\rho} \frac{dp}{dx} = -\frac{du}{dt} + \nu \nabla^2 u - \frac{1}{2} \frac{d(u^2 + v^2)}{dx} - v \left( \frac{du}{dy} - \frac{dv}{dx} \right), \quad (1)$$

$$\frac{1}{\rho} \frac{dp}{dy} = -\frac{dv}{dt} + \nu \nabla^2 v - \frac{1}{2} \frac{d(u^2 + v^2)}{dy} - u \left( \frac{du}{dy} - \frac{dv}{dx} \right) - g, \quad (2)$$

where  $y$  is measured vertically upwards, and  $\nu (= \mu/\rho)$  is the kinematic viscosity. Since the fluid is supposed to be incompressible,

$$\frac{du}{dx} + \frac{dv}{dy} = 0; \quad (3)$$

or what is equivalent,

$$u = d\psi/dy, \quad v = -d\psi/dx, \quad (4)$$

$\psi$  being the stream-function.

In virtue of (4), we have in (1), (2)

$$\frac{du}{dy} - \frac{dv}{dx} = \nabla^2 \psi. \quad (5)$$

It may be well to commence with the comparatively simple question of stationary waves, carried to the second order of approximation, when viscosity is neglected. If we eliminate  $p$  from (1) and (2), putting at the same time  $\nu = 0$ , we find

$$-\frac{d}{dt} \nabla^2 \psi = u \frac{d\nabla^2 \psi}{dx} + v \frac{d\nabla^2 \psi}{dy}. \quad (6)$$

As was to be expected from the general theory of a frictionless fluid, the solution of (6) to any order of approximation is

$$\nabla^2 \psi = 0. \quad (7)$$

We now assume that the motion is periodic with respect to  $x$ —proportional, say, to  $\cos kx$ , so far as the first approximation is concerned. Thus for this approximation we take

$$\psi = Ae^{ky} \cos kx \cos nt, \quad (8)$$

the term in  $e^{-ky}$ , otherwise admissible, being excluded by the consideration that all motion must vanish when  $y = -\infty$ , inasmuch as the fluid is supposed infinitely deep. Corresponding to (8),

$$u = d\psi/dy = kAe^{ky} \cos kx \cos nt \quad (9)$$

$$v = -d\psi/dx = kAe^{ky} \sin kx \cos nt, \quad (10)$$

so that

$$u^2 + v^2 = k^2 A^2 e^{2ky} \cos^2 nt. \quad (11)$$

In virtue of (5), (7), the equations of pressure become

$$\begin{aligned} \frac{1}{\rho} \frac{dp}{dx} &= -\frac{du}{dt} - \frac{1}{2} \frac{d(u^2 + v^2)}{dx}, \\ \frac{1}{\rho} \frac{dp}{dy} &= -\frac{dv}{dt} - \frac{1}{2} \frac{d(u^2 + v^2)}{dy} - g; \end{aligned}$$

and thus

$$p/\rho = -gy + nAe^{ky} \sin kx \sin nt - \frac{1}{2} k^2 A^2 e^{2ky} \cos^2 nt + f(t), \quad (12)$$

where  $f(t)$  denotes a function of  $t$  which is arbitrary so far as the differential equations of pressure are concerned. The pressure at the surface is to be found from (12) by putting  $y = \eta$ , where  $\eta$  is the elevation of the surface at the point in question. The relation between  $\eta$  and  $u, v$  is thus required accurately to the second order of small quantities.

The differential relation\* is

$$\frac{d\eta}{dt} = v - u \frac{d\eta}{dx}. \quad (13)$$

To the first order we have  $d\eta/dt$  equal simply to the value of  $v$  at the surface, so that by (10)

$$\eta = kn^{-1}A \sin kx \sin nt, \quad (14)$$

the origin of  $y$  being in the undisturbed surface. This value of  $\eta$  may be used in the small terms of (13), and thus to a second approximation

$$\eta = \frac{kA}{n} \sin kx \sin nt + \frac{k^3 A^2}{4n^3} \cos 2kx \cos 2nt + F(x), \quad (15)$$

where  $F(x)$  is an arbitrary function of  $x$  of the second order of small quantities.

We are now prepared to substitute for  $y$  its value  $\eta$  in (12). In the principal term we must use the complete value of  $\eta$  from (15). In the second term, already containing  $A$  as a factor, the first approximation for  $\eta$  suffices, while in the third term we may put  $\eta = 0$ . The third term thus becomes a function of  $t$  only, and may be regarded as cancelled by  $f(t)$ . We find

$$\begin{aligned} \frac{p}{\rho} = & A \left( n - \frac{gk}{n} \right) \sin kx \sin nt - \frac{k^2 A^2}{4} \cos 2kx \\ & + \frac{k^2 A^2}{4} \left( 1 - \frac{gk}{n^2} \right) \cos 2kx \cos 2nt - g F(x). \end{aligned} \quad (16)$$

In free vibrations the condition to be satisfied at the surface is  $p = 0$ . The annullment of the term in  $nt$  requires that

$$n^2 = gk, \quad (17)$$

and the same well-known relation suffices to annul the term in  $2nt$ . The surface condition is satisfied without any addition to  $\psi$ , if besides satisfying (17) we identify  $g F(x)$  with  $-\frac{1}{4}k^2 A^2 \cos 2kx$ . Thus, writing  $A'$  for  $kA/n$ , we obtain, as the complete value of  $\eta$ ,

$$\eta = A' \sin kx \sin nt + \frac{1}{4}kA'^2 \cos 2kx \cos 2nt - \frac{1}{4}kA'^2 \cos 2kx. \quad (18)$$

We now proceed with the consideration of the problem when viscosity

\* Cf. Lamb's 'Hydrodynamics,' § 10.



is retained. Eliminating  $p$  from (1) and (2), we get, with use of (3) and (5),

$$\nabla^4 \psi - \frac{1}{\nu} \frac{d}{dt} \nabla^2 \psi = \frac{u}{\nu} \frac{d \nabla^2 \psi}{dx} + \frac{v}{\nu} \frac{d \nabla^2 \psi}{dy}. \quad (19)$$

The terms on the right hand of (19) are of the second order in the amplitude of vibration, and thus for the first approximation we have simply

$$\nabla^4 \psi - \frac{1}{\nu} \frac{d}{dt} \nabla^2 \psi = 0. \quad (20)$$

The solution of (20) may be written

$$\psi = \psi_1 + \psi_2, \quad (21)$$

$$\text{where} \quad \nabla^2 \psi_1 = 0, \quad \left( \nabla^2 - \frac{1}{\nu} \frac{d}{dt} \right) \psi_2 = 0. \quad (22)$$

We now introduce the suppositions that in the first approximation  $\psi_1$ ,  $\psi_2$  are proportional to  $\cos kx$ , and also to  $e^{int}$ . The wave-length along  $x$  is  $2\pi/k$ , and the period  $\tau$  is  $2\pi/n$ . The equations (20) now become

$$\left( \frac{d^2}{dy^2} - k^2 \right) \psi_1 = 0, \quad \left( \frac{d^2}{dy^2} - k^2 - \frac{in}{\nu} \right) \psi_2 = 0, \quad (23)$$

by which  $\psi_1$  and  $\psi_2$  are to be determined as functions of  $y$ . If we write

$$k'^2 = k^2 + in/\nu, \quad (24)$$

we have, as the most general solutions of (23),

$$\psi_1 = A'e^{ky} + B'e^{-ky}, \quad \psi_2 = C'e^{k'y} + D'e^{-k'y}; \quad (25)$$

but if the real part of  $k'$  is taken positive, the terms in  $B'$  and  $D'$  are excluded when the fluid is treated as infinitely deep. Thus for our purpose

$$\psi_1 = A e^{ky} \cos kx e^{int}, \quad \psi_2 = C e^{k'y} \cos kx e^{int}, \quad (26)$$

where  $A$  and  $C$  are now absolute constants, real or complex. We shall presently find it convenient to suppose  $C$  real. From (4) we now find

$$u = (kAe^{ky} + k'Ce^{k'y}) \cos kx e^{int}, \quad (27)$$

$$v = (kAe^{ky} + kCe^{k'y}) \sin kx e^{int}; \quad (28)$$

and since to this approximation  $d\eta/dt = v$ ,

$$\eta = (k/in)(A + C) \sin kx e^{int}. \quad (29)$$

If we omit the terms of the second order in (1), we find

$$\frac{1}{\rho} \frac{dp}{dx} = -\frac{d}{dy} \left( \frac{d\psi_1}{dt} + \frac{d\psi_2}{dt} \right) + \nu \frac{d}{dy} (\nabla^2 \psi_1 + \nabla^2 \psi_2) = -\frac{d}{dy} \frac{d\psi_1}{dt},$$

in virtue of (22); and in like manner

$$\frac{1}{\rho} \frac{dp}{dy} = \frac{d}{dx} \frac{d\psi_1}{dt} - g.$$

Hence 
$$\frac{p}{\rho} = -gy + \int \left( \frac{d^2\psi_1}{dx dt} dy - \frac{d^2\psi_1}{dy dt} dx \right), \quad (30)$$

the expression to be integrated being a perfect differential by (22).

Applying (30) to the present case, we find

$$p/\rho = -gy - inAe^{ky} \sin kx e^{int}. \quad (31)$$

At the surface we are to suppose  $y = \eta$ , and  $\eta$  may be neglected in the term already multiplied by  $A$ . Thus at the surface

$$\frac{p}{\rho} = i \left\{ \frac{gk}{n} (A + C) - nA \right\} \sin kx e^{int}. \quad (32)$$

Now that we have to reckon with viscosity, the stress conditions at the surface can no longer be expressed merely by  $p$ . In the usual notation, applicable also in the theory of elastic solids,  $p_{xx}$ ,  $p_{yy}$  denote normal tractions across faces perpendicular to  $x$  and  $y$  respectively, while  $p_{xy}$  denotes the tangential traction which acts parallel to  $y$  across the face perpendicular to  $x$ , or the equal traction parallel to  $x$  across the face perpendicular to  $y$ . The expressions for these tractions are\*

$$p_{xx} = -p + 2\mu \frac{du}{dx}, \quad p_{yy} = -p + 2\mu \frac{dv}{dy}, \quad (33)$$

$$p_{xy} = \mu \left( \frac{dv}{dx} + \frac{du}{dy} \right). \quad (34)$$

When viscosity was neglected, we were able to suppose that the surface of the fluid was entirely free from imposed force. Under such circumstances the vibrations of a viscous fluid could not be maintained. If  $n$  is to be real, some maintaining forces are necessary. We will suppose that these forces are exclusively normal in their character, and accordingly make  $p_{xy} = 0$ ; for it is to be observed that in the present approximation a direction parallel to the surface may be identified with the horizontal. By (27), (28), (34) we find, making  $y = 0$ ,

$$2k^2A + (k^2 + k'^2)C = 0, \quad (35)$$

as the condition of no tangential force at the surface. Or, if we substitute for  $k'^2$  its value from (24), (35) becomes

$$A + \left( 1 + \frac{in}{2k^2\nu} \right) C = 0. \quad (36)$$

For the normal traction at the surface we have from (33),

$$\begin{aligned} n p_{yy}/\rho &= A \{ i(n^2 - kg) + 2\nu k^2 n \} \sin kx e^{int} \\ &+ C \{ -ikg + 2\nu k k' n \} \sin kx e^{int}, \end{aligned} \quad (37)$$

\* Cf. Lamb's 'Hydrodynamics,' § 314.

and by (36) the expression for  $\eta$  in (29) may be written

$$\eta = -\frac{C}{2k\nu} \sin kx e^{int}. \quad (38)$$

These equations constitute the complete symbolical solution of the problem of infinitely small stationary waves maintained by purely normal surface pressures in a fluid of any degree of viscosity.\*

In preparing to pass to real quantities, it is simplest to suppose  $C = -2k\nu$ , so that

$$\eta = \sin kx e^{int}. \quad (39)$$

$A$  is then given explicitly by (36), and on substitution in (37) we get

$$p_{yy}/\rho = \{g - n^2/k + 4i\nu nk + 4\nu^2 k^2 (k - k')\} \sin kx e^{int}. \quad (40)$$

The passage to real quantities is now only complicated by the term in  $k'$ . If the viscosity be small, this term may be omitted, and we may take

$$p_{yy}/\rho = \{g - n^2/k + 4i\nu nk\} \sin kx e^{int} = (g - n^2/k) \eta + 4\nu k \cdot d\eta/dt, \quad (41)$$

giving the normal traction necessary to maintain the waves represented by  $\eta = \sin kx \cos nt$ . If  $n^2 = gk$ , the part of  $p_{yy}$  in the same phase as  $\eta$  disappears, and

$$p_{yy} = 4\mu k \cdot d\eta/dt \quad (42)$$

simply. It is to be remembered that  $p_{yy}$  is a *traction*. If, as is usual in hydrodynamics, we use pressure ( $p'$ ), we see that the pressure has its maximum value when the surface is *falling* fastest, as was to be expected.

The accurate expression for the real part of (40) may, of course, be formed. If in (24) we put

$$k^2 = P^2 \cos 2\alpha, \quad n/\nu = P^2 \sin 2\alpha, \quad (43)$$

then

$$k' = P \cos \alpha + i P \sin \alpha. \quad (44)$$

It is unnecessary to write down the actual form of the real part of (40). In most applications an approximate value of  $k'$  suffices. On account of the smallness of  $\nu$ ,  $n/\nu$  is very large in comparison with  $k^2$ , that is to say, the thickness of the stratum through which the tangential motion can be propagated in time  $\tau$  is very small relatively to the wave-length  $\lambda$ . We may, therefore, usually neglect  $k^4$  in the equation

$$P^4 = k^4 + n^2/\nu^2, \quad (45)$$

and take simply

$$P^2 = n/\nu. \quad (46)$$

$$\text{Again,} \quad (\sin \alpha - \cos \alpha)^2 = 1 - \sin 2\alpha = \frac{1}{2} k^4 \nu^2 / n^2, \quad (47)$$

so that the difference between  $\cos \alpha$  and  $\sin \alpha$  may often be neglected.

\* Cf. Basset's 'Hydrodynamics,' § 520; Lamb, *loc. cit.*, § 332.

It appears that the terms neglected in (40) when (41) is substituted are of the order  $\nu^{3/2}$ .

In proceeding to a second approximation we have first to calculate the terms of the second order forming the right-hand member of (19), using the values found in the first approximation. In these

$$\nabla^2 \psi = \nabla^2 \psi_2 = \frac{1}{\nu} \frac{d\psi_2}{dt} = \frac{inC}{\nu} e^{ky} \cos kx e^{int},$$

whence, the imaginary part being rejected,

$$\frac{d\nabla^2 \psi}{dx} = \frac{knC}{\nu} \sin kx e^{P \cos \alpha \cdot y} \sin (nt + P \sin \alpha \cdot y) \quad (48)$$

$$\frac{d\nabla^2 \psi}{dy} = -\frac{nPC}{\nu} \cos kx e^{P \cos \alpha \cdot y} \sin (nt + P \sin \alpha \cdot y + \alpha). \quad (49)$$

Also, in real quantities by (27), (28), (36),

$$u = C \cos kx \left\{ k e^{ky} \left( -\cos nt + \frac{n}{2k^2 \nu} \sin nt \right) + P e^{P \cos \alpha \cdot y} \cos (nt + P \sin \alpha \cdot y + \alpha) \right\}, \quad (50)$$

$$v = kC \sin kx \left\{ e^{ky} \left( -\cos nt + \frac{n}{2k^2 \nu} \sin nt \right) + e^{P \cos \alpha \cdot y} \cos (nt + P \sin \alpha \cdot y) \right\}. \quad (51)$$

Hence

$$\begin{aligned} & \frac{2\nu (u d\nabla^2 \psi / dx + v d\nabla^2 \psi / dy)}{nkC^2 \sin kx \cos kx e^{P \cos \alpha \cdot y}} \\ &= -k e^{ky} \{ \sin (2nt + P \sin \alpha \cdot y) + \sin (P \sin \alpha \cdot y) \} \\ &+ \frac{n e^{ky}}{2k\nu} \{ \cos (P \sin \alpha \cdot y) - \cos (2nt + P \sin \alpha \cdot y) \} \\ &+ P e^{ky} \{ \sin (2nt + P \sin \alpha \cdot y + \alpha) + \sin (P \sin \alpha \cdot y + \alpha) \} \\ &- \frac{nP e^{ky}}{2k^2 \nu} \{ \cos (P \sin \alpha \cdot y + \alpha) - \cos (2nt + P \sin \alpha \cdot y + \alpha) \} \\ &- 2P e^{P \cos \alpha \cdot y} \sin \alpha. \end{aligned} \quad (52)$$

By (19) the equation with which we have to deal is

$$\nabla^4 \psi - \frac{1}{\nu} \frac{d}{dt} \nabla^2 \psi = \frac{nkC^2 \sin 2kx}{4\nu^2} \times e^{P \cos \alpha \cdot y} \times \text{right-hand member of (52)}. \quad (53)$$

It will be observed that in (52) or (53) the terms on the right, regarded as functions of  $t$ , are either independent of  $t$  or circular functions of  $2nt$ . Corresponding terms, proportional also to  $\sin 2kx$ , will appear in the direct

integral of (53), and in addition we must include a "complementary function" representing, so far as required, the complete integral of (53) when the second member is made equal to zero. This part contains the terms of the first approximation (26), which now represent themselves; and we must also be prepared to admit terms of the second order proportional to  $\sin 2kx$ , and either independent of time or involving  $2nt$ . In the former case the differential equation reduces to

$$\nabla^4 \psi = \left( \frac{d^2}{dy^2} - 4k^2 \right)^2 \psi = 0, \quad (54)$$

giving as the solution applicable to deep water,

$$\psi = \sin 2kx (H + Ky) e^{2ky}, \quad (55)$$

where  $H$  and  $K$  are constants. A term in  $K$  would represent vortices of the kind found in the former paper to arise from the action of the bottom (when the liquid is not too deep); and one of the principal objects of the present investigation is to ascertain whether these terms occur as the result of the conditions operative at the free surface. It may be recalled that though such vortices could not arise in an ideal frictionless fluid, their magnitude, when fully established, may be independent of the amount of the friction. In view of the complication of the problem it must suffice to limit the investigation to the case of *small* viscosity, the question being whether vortices can be maintained when the viscosity is reduced without limit.

On the right of (52) there are nine terms, of which five are independent of  $t$ . But they are not of equal importance. Since  $P$  is of the order  $\nu^{-1}$ , the leading term is the seventh in order. So far as this term is concerned,

$$\left( \frac{d^2}{dy^2} - 4k^2 \right)^2 \psi = -\frac{n^2 PC^2 \sin 2kx}{8k\nu^3} \cdot e^{ky} e^{P \cos \alpha \cdot y} \cos (P \sin \alpha \cdot y + \alpha).$$

It is now convenient to revert to complex quantities, regarding  $e^{P \cos \alpha \cdot y} \cos (P \sin \alpha \cdot y + \alpha)$  as the real part of  $e^{ky + i\alpha}$ . Thus

$$\left( \frac{d^2}{dy^2} - 4k^2 \right)^2 \psi = -\frac{k' n^2 C^2 \sin 2kx}{8k\nu^3} \cdot e^{(k'+k)y},$$

giving 
$$\psi = -\frac{k' n^2 C^2 \sin 2kx}{8k\nu^3 \{(k'+k)^2 - 4k^2\}^2} e^{(k'+k)y}. \quad (56)$$

To form the surface condition, representing the evanescence of tangential force, we shall require the expression of

$$\frac{du}{dy} + \frac{dv}{dx} = \frac{d^2 \psi}{dy^2} - \frac{d^2 \psi}{dx^2} = \{(k'+k)^2 + 4k^2\} \psi,$$

in which, since  $C^2$  is already involved as a factor, we may put  $y = 0$ . Thus

$$\frac{du}{dy} + \frac{dv}{dx} = -\frac{k'n^2 C^2 \sin 2kx \{(k' + k)^2 + 4k^2\}}{8k\nu^3 \{(k' + k)^2 - 4k^2\}^2}, \quad (57)$$

from which the imaginary part is to be rejected.

In tracing the value of (57) as  $\nu$  diminishes, we get ultimately

$$-\frac{n^2 C^2 \sin 2kx}{8kk'\nu^3}. \quad (58)$$

In this  $C^2/\nu^3$  is of the order  $A^2$ , and  $k'$  is of order  $\nu^{-\frac{1}{2}}$ , so that (58) is of order  $\nu^{-\frac{1}{2}}A^2$ , becoming infinite in comparison with  $A^2$ , as  $\nu$  diminishes without limit. We shall find, however, that this infinite term is compensated by another, to be brought forward later. For our purpose we must retain all terms which do not vanish with  $\nu$  in comparison with  $A^2$ . Hence, with sufficient approximation,

$$\frac{k' \{(k' + k)^2 + 4k^2\}^{\frac{1}{2}}}{\nu \{(k' + k)^2 - 4k^2\}^2} = \frac{k'}{\nu(k' + k)^2} = \frac{1}{\nu k'} - \frac{2k}{\nu k'^2} = \frac{1}{\nu k'} - \frac{2k}{in + \nu k^2} = \frac{1}{\nu k'} + \frac{2ik}{n},$$

of which the second term, being purely imaginary, is to be rejected. Thus

$$\frac{du}{dy} + \frac{dv}{dx} = \text{real part of } -\frac{n^2 C^2 \sin 2kx}{8kk'\nu^3} = -\frac{n^2 C^2 \cos \alpha \sin 2kx}{8k\nu^3 P}. \quad (59)$$

Referring back to (52) and having regard to the orders of the various terms in respect of  $\nu$ , we see that the only other term independent of  $t$  which needs be retained is the third in order of arrangement. From this term we obtain in like manner,

$$\psi = \frac{n^2 C^2 \sin 2kx}{8\nu^3} \frac{e^{(k' + k)y}}{\{(k' + k)^2 - 4k^2\}^2}, \quad (60)$$

and when  $y = 0$ ,

$$\frac{du}{dy} + \frac{dv}{dx} = \frac{n^2 C^2 \sin 2kx}{8\nu^3} \frac{(k' + k)^2 + 4k^2}{\{(k' + k)^2 - 4k^2\}^2} = \frac{n^2 C^2 \sin 2kx}{8\nu^2 k'^2} \quad (61)$$

with sufficient approximation.

In (61),  $\nu k'^2$ , so far as it need be retained, is a pure imaginary, and accordingly there is no contribution from this source. We are left therefore with (59) as the complete contribution of the direct integral of (53) when  $\nu = 0$ , so far as the terms independent of  $t$  are concerned.

In a similar manner we may treat the terms in  $2nt$ . We find for the leading term

$$\nabla^4 \psi - \frac{1}{\nu} \frac{d}{dt} \nabla^2 \psi = \text{real part of } \frac{k' \cdot n^2 C^2 \sin 2kx}{8k\nu^3} e^{(k' + k)y} e^{2int};$$

so that, if we finally reject the imaginary part,

$$\frac{du}{dy} + \frac{dv}{dx} = \frac{n^2 C^2 \sin 2kx e^{2int}}{8k\nu^2} \left( -\frac{1}{\nu k'} + \frac{2ik}{n} \right), \quad (62)$$

when  $y = 0$ . And for the only other term which it is necessary to retain,

$$\frac{du}{dy} + \frac{dv}{dx} = \frac{nC^2}{8\nu^2} \sin 2kx \sin 2nt. \quad (63)$$

We have now sufficiently complete expressions for  $du/dy + dv/dx$  so far as it results from the direct integral of (53). But to these we have to add terms arising from the complementary function. In this there must, at any rate, be included the terms in  $nt$  found in the first approximation. From (27), (28) we get, when  $y$  is small,

$$\frac{du}{dy} + \frac{dv}{dx} = \cos kx \cdot e^{int} \{2k^2 A + (k^2 + k'^2) C + 2k^2 A \cdot ky + (k^2 + k'^2) C \cdot k'y\}, \quad (64)$$

and in this we are to substitute for  $y$  the value  $\eta$  appropriate to the surface. In the first approximation the terms containing  $y$  were neglected, and the surface condition gave

$$2n^2 A + (k^2 + k'^2) C = 0. \quad (65)$$

This relation must still hold, approximately at any rate. Using it in the small terms of (64), we get

$$(k'^2 + k^2) C (k' - k) y \cos kx e^{int},$$

in which we may neglect  $k$  in comparison with  $k'$ . Passing to real quantities, we find

$$-\frac{nPC}{\nu} y \cos kx \sin (nt + \alpha).$$

The real value of  $y$ , or  $\eta$  from (38), is

$$\eta = -\frac{C}{2k\nu} \sin kx \cos nt, \quad (66)$$

so that this part of (64) becomes

$$\frac{du}{dy} + \frac{dv}{dx} = \frac{nPC^2}{8k\nu^2} \sin 2kx \{\sin (2nt + \alpha) + \sin \alpha\}. \quad (67)$$

Thus for the terms independent of  $t$  we get, from (59), (67),

$$\frac{du}{dy} + \frac{dv}{dx} = \frac{nC^2 \sin 2kx}{8k\nu^2} \left\{ -\frac{n \cos \alpha}{P\nu} + P \sin \alpha \right\}. \quad (68)$$

The factor within braces vanishes with  $\nu$ , as may be proved from (43), the two infinite terms cancelling without finite residue. Thus altogether  $du/dy + dv/dx$  vanishes with  $\nu$  so far as the terms independent of  $t$  are concerned.

The terms in  $2nt$  are of less interest. We find, in the same way, when  $\nu$  is diminished without limit for the complete value of  $du/dy + dv/dx$  at the surface,

$$-\frac{n C^2 \sin 2kx \sin 2nt}{8\nu^2}. \quad (69)$$

But we are not yet in a position to apply the condition which must be satisfied at the surface, viz., that the tangential force shall there vanish; for we must remember that the surface can no longer be treated as parallel to  $y = 0$ . If  $\theta$  be the angle which the surface at the point under consideration makes with  $y = 0$ , the formulæ of transformation are

$$\begin{aligned} p_{x'x'} &= \cos^2 \theta p_{xx} + \sin^2 \theta p_{yy} + \sin 2\theta p_{xy}, \\ p_{y'y'} &= \sin^2 \theta p_{xx} + \cos^2 \theta p_{yy} - \sin 2\theta p_{xy}, \\ p_{x'y'} &= (\cos^2 \theta - \sin^2 \theta) p_{xy} + \sin \theta \cos \theta (p_{yy} - p_{xx}). \end{aligned}$$

For the present purpose  $\theta$  may be regarded as a small quantity, equal to  $\pm d\eta/dx$ , whose square may be neglected, and we may take

$$p_{x'y'} = p_{xy} + \theta (p_{yy} - p_{xx}). \quad (70)$$

It is  $p_{x'y'}$ , and not  $p_{xy}$ , which is to be made to vanish to the second order of the vibration.

The expressions for  $p_{xx}$ , etc., have already been given in (33), (34). Substituting the values of  $u, v$  of the first approximation, we find, when  $\nu$  is small,

$$-2 \left( \frac{du}{dx} - \frac{dv}{dy} \right) = \frac{2nC}{\nu} \sin kx \sin nt, \quad (71)$$

and

$$\frac{d\eta}{dx} = -\frac{C}{2\nu} \cos kx \cos nt. \quad (72)$$

It appears, then, that so far as the terms independent of  $t$  are concerned, there is no difference between  $p_{x'y'}$  and  $p_{xy}$ , and since we have already seen that  $p_{xy}$  vanishes, it follows that the surface condition of no tangential force is satisfied to a second approximation, without the addition of any further terms (55), such as would represent permanent vortices. Accordingly, no such vortices exist.

As regards terms in  $2nt$ , we find in addition to (69) another term of the same form derived from (71) and (72). In a solution complete to the second order these terms would need to be compensated by the introduction of new second-order terms in  $\psi$  of the form

$$\psi = (Le^{2ky} + Me^{k''y}) \sin 2kx e^{2int}, \quad (73)$$

where

$$k''^2 = 4k^2 + 2in/\nu; \quad (74)$$

but it is scarcely necessary for our purpose to define them further. Neither does it seem worth while to express at length the equation of pressure when the second-order terms are included. The particular case of no viscosity already considered illustrates the procedure. Terms in the expression of the pressure which are independent of  $t$  are balanced by corresponding terms in  $\eta$  not affecting the velocities.



*On the Accumulation of Helium in Geological Time.*

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In a former paper\* I gave an account of experiments on the presence of helium in a variety of the common minerals of the earth's crust. The conclusion arrived at was that the quantity of helium is, in general, determined by the traces of radio-active elements present. The minerals investigated were mostly of palæozoic age, and little attention was paid to the effect of geological age on helium content. If, however, the accepted theory of the progressive accumulation of helium in minerals by radio-active change is correct, it is evident that geological age must be all-important. In the present paper, the subject is considered from that point of view.

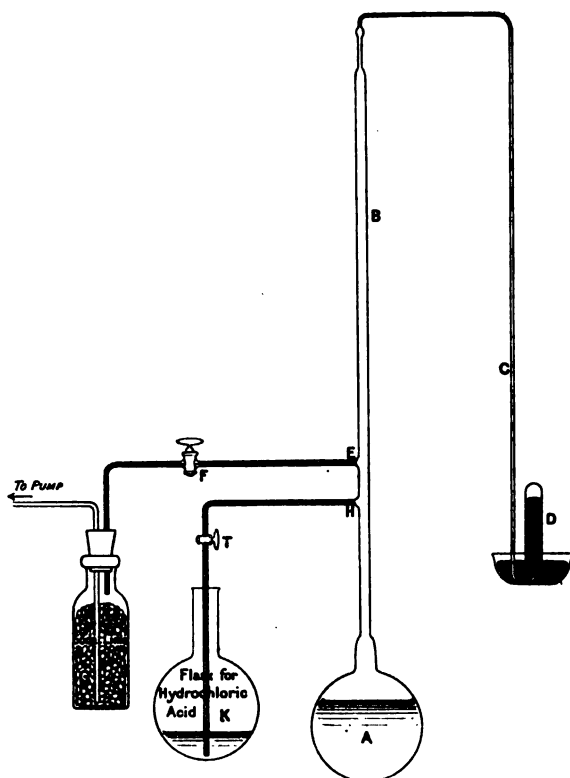
There is some difficulty in finding suitable material for comparing the helium content of minerals with their geological age. To make such a comparison advantageously, it is necessary to obtain minerals from a very great range of geological horizons, so that the oldest minerals considered shall be many times older than the youngest. Thus it becomes imperative to get material from the secondary and tertiary strata. Most of the constituents of these strata are unsuitable. For instance, derivative materials like clay and sand must be rejected, because they have presumably been accumulating helium long before they were laid down in their present stratigraphical position. The chemical precipitates like rocksalt and gypsum are so free from radio-active constituents that accurate measurements of the helium in them are very difficult; while limestones are, in a lesser degree, open to the same objection.

In view of these difficulties, I have been fortunate in discovering that phosphatic nodules (the so-called coprolites) and phosphatised bones are extremely rich in radio-active constituents, sometimes containing 50 times as much radium as the generality of rocks. These nodules and bones are found in a great variety of strata, from the pliocene downwards. The nodules frequently contain, or consist of, fossils characteristic of the stratum to which they belong, or of one very little earlier; thus their age is well defined. The same remark applies still more to the mineralised bones. There is no reason to doubt that the radio-active material was introduced into the bones by infiltration at the time that they became phosphatised; and from that epoch the accumulation of helium must be dated.

\* 'Roy. Soc. Proc.,' A, vol. 80, 1908, p. 572.

In these experiments I have extracted the helium by solution of the powdered substance in hydrochloric acid. The action takes place quite readily.

The apparatus used is shown in the figure.



The powdered mineral (usually from 100 to 500 grammes) is placed in the flask A, which is then sealed on to the rest of the apparatus. The system of tubes is evacuated through stopcock F, and washed out with a little oxygen to secure more perfect removal of air. Hydrochloric acid (which has been well boiled, and closed up so as to cool in absence of air) is then admitted through T. A violent effervescence of carbon dioxide follows. The gas is allowed to flow into the pump through F, by means of which the flow is regulated. On its way it traverses a bottle filled with soda lime, and in some cases a tube of hot copper oxide, followed by caustic potash. By these reagents the bulk of the carbon dioxide is absorbed, as are also small quantities of combustible gases which accompany it. A small residue, consisting chiefly of nitrogen, is collected through the pump. When the flask A is three-quarters full of acid, and the effervescence is nearly over, the stopcocks

F and T are closed, and A heated to boiling. The gases expelled pass up into the top of B, while the lower portion is filled with steam, which condenses and runs back. When boiling has gone on long enough to ensure complete expulsion of the dissolved gas, the heat is increased, so that the outflow of steam exceeds what B can condense. The gas then passes out at the lower end of C, where it is collected over mercury in D as shown. It is followed by steam, which condenses and forms pistons in C. By removing D at the right moment it is easy to make an exact separation of the gas from the condensed water which follows it. The gas collected in this way is added to that collected through the pump, and the inert constituents isolated by sparking with oxygen in the usual way. The gas was examined and measured substantially as described in the former paper.

I have found that in practice it is much more difficult to avoid contamination with air when the material is dissolved in acid than when it is merely heated. Thus argon was usually conspicuous in the spectrum of the inert residue; and on cooling the charcoal neon was sometimes visible, when it was not masked by a large excess of helium. Elaborate arrangements for boiling the acid *in vacuo* and admitting it without contact with the atmosphere would probably overcome this difficulty; but it was not judged worth while to adopt them, as helium is readily isolated for measurement by the charcoal method. The great advantage of dissolving the material rather than merely heating it is in the certainty of extracting all the helium.

In measuring quantities of helium less than a cubic millimetre, the method of sparking in a tube with sodium-potassium electrodes, followed by absorption with charcoal cooled in solid carbon dioxide, is inadequate. It is found that even with no helium present in the original gas the residue after this treatment is a fraction (say  $1/3$ ) of a cubic mm. It would seem that hydrogen, which is almost always present in discharge tubes, is not perfectly absorbed by the sodium-potassium electrodes, but exerts a kind of vapour pressure. This hydrogen is not absorbed by charcoal at  $-80^{\circ}\text{C}$ . By cooling the charcoal in liquid air, the residue (in a blank experiment) can be reduced below  $1/100$  cubic mm.

It must be admitted that hydrogen was scarcely if at all visible in the spectrum of the discharge, when the tube had been run for some time. However, in spite of this, I think the above explanation of the residue is the most probable that can be suggested.

When very small quantities of helium were to be measured, liquid air cooling was generally made use of. In cases where no liquid air was at hand, and when the experiment did not appear to be worth pursuing further, the quantity of helium was recorded as a maximum only.

Radium was determined by the methods described in earlier papers. The

solution obtained in extracting helium was usually employed for the radium determination.

The uranium oxide percentage was calculated from the radium observations, by standardisation with a uranium mineral. It will be observed that this method does not involve a knowledge of the ratio of uranium to radium in minerals, but only assumes its constancy.

The results may be tabulated as follows:—

Material.	Locality.	Geological horizon.	Helium, c.c.m. per 100 grammes.	U <sub>3</sub> O <sub>8</sub> , grammes per 100 grammes.	Helium, c.c. per gramme of U <sub>3</sub> O <sub>8</sub> .
Phosphatised shark's teeth	Florida .....	Pliocene .....	0·174	$2\cdot48 \times 10^{-2}$	0·0070
Phosphatised Cetacean bones	Felixstowe .....	Pliocene Red Crag	0·158	$1\cdot55 \times 10^{-2}$	0·0102
Phosphatic nodules .....	" .....	" "	0·098	$4\cdot78 \times 10^{-3}$	0·0205
" " .....	Cambridge .....	Upper Greensand	3·03	$1\cdot08 \times 10^{-2}$	0·281
" " .....	Potton, Bedford- shire	Lower Greensand	2·10	$5\cdot83 \times 10^{-3}$	0·360
Phosphatised Saurian bones	Ely .....	Kimmeridge Clay	<0·365	$3\cdot28 \times 10^{-3}$	<0·111
Phosphatic nodules .....	Knapwell, Cambs.	Base of Kimme- ridge Clay	<0·675	$7\cdot20 \times 10^{-3}$	<0·094
Phosphatised Saurian bones	Whittlesea .....	Oxford Clay .....	<0·51	$9\cdot15 \times 10^{-4}$	<0·558
Phosphatic bone frag- ments	Lyme Regis .....	Rhætic bone bed	<0·22	$2\cdot15 \times 10^{-3}$	<0·102
Hæmatite .....	Frizington, by Carnforth, Cum- berland	Above carboni- ferous limestone	16·5	$1\cdot28 \times 10^{-3}$	12·9
Phosphatic nodules .....	Near Bala .....	Bala beds .....	15·3	$3\cdot23 \times 10^{-3}$	4·74
Phosphatic limestone ...	Chirbury, Shrop- shire	Llandeilo lime- stone	5·6	$7\cdot90 \times 10^{-4}$	7·10
Phosphatic nodules .....	Cailleach Head, Loch Broom	Torridon Sand- stone	0·83	$9\cdot9 \times 10^{-4}$	0·84

It will be at once noticed that the order of stratigraphical position is not accurately followed. For example, the phosphatic nodules and bones from the Kimmeridge Clay do not show so high a helium ratio as those from the Lower or Upper Greensand, though they are geologically older than either. At the same time it will be noticed that helium ratios approaching 12, such as are common in the mineral veins of carboniferous age in Cornwall, are not met with in the younger strata.\* The facts are most easily explained by supposing that the retention of helium has been often if not always imperfect.

One point remains to be referred to. If thorium were present in any of these materials we might expect it to have a disturbing influence, as an

\* Examples will be found in 'Roy. Soc. Proc.,' A, vol. 80, p. 573. I have not reprinted the values here, as they were only obtained by the crude method of heating the minerals. This, however, suffices to give the order of magnitude.

independent source of helium. The most searching experiments I have been able to make have only suggested a faint suspicion of its presence in the phosphatic nodules and bones. It can contribute nothing appreciable to their activity. The same applies to Cumberland hæmatite; in this case the results were still more distinctly negative. I have included this mineral in the investigation as it is one of the few readily dissolved in hydrochloric acid. There is, of course, a very large field of research open in accurately determining the helium ratio for other minerals such as the metallic sulphides, but I have not yet had leisure to give any attention to them. Great interest will attach to determining the highest ratio to be found among minerals of Archæan age; but here the presence of thorium enters as a complication.

The chief interest of the present results is in their application to the measurement of geological time. For this application we require to know the rate at which helium is produced from 1 gramme of uranium with the equilibrium quantity of all the other products of the series. No direct measurements of this have yet been made; I believe, however, that such measurements are quite feasible, and hope eventually to supply them. In the meantime it is interesting to calculate, as nearly as possible from indirect data, the time required for the accumulation of such quantities of helium as are found.

Professor Rutherford has kindly communicated to me his latest estimate. It is that 316 cubic mm. of helium are produced per gramme of radium per annum. This is deduced on the following assumptions:—

(1) The number of helium atoms produced is equal to the number of  $\alpha$ -particles emitted.

(2) For every four  $\alpha$ -particles emitted by radium with its immediate products, two are emitted by uranium, one by ionium, and one by polonium.

I shall not enter on any discussion of the validity of these suppositions, beyond remarking that there are no definite grounds at present for deciding whether or not helium is liberated in the rayless changes.

Taking the ratio of radium to uranium in minerals as  $3.4 \times 10^{-7}$ , we get for the annual helium production per gramme of uranium oxide, ( $U_3O_8$ ), in a mineral,  $9.13 \times 10^{-8}$  c.c.

Adopting this rate of growth provisionally, the following ages are obtained as a minimum for some of the materials examined:—

	Years.
Phosphatic nodules of the Crag .....	225,000
Phosphatic nodules of the Upper Greensand .....	3,080,000
Phosphatic nodules of the Lower Greensand .....	3,950,000
Hæmatite overlying carboniferous limestone .....	141,000,000

It must be emphatically repeated that these absolute values are provisional only. I hope that geologists and others will not regard the method as discredited if it should be necessary to alter them considerably, when the rate of growth of helium has been directly determined.

The conclusions of this paper may be summarised as follows :—

1. Phosphatic nodules and phosphatised bones of all geological ages possess marked radio-activity, many times higher than that of rocks. This activity is due to products of the uranium series.

2. Helium has been detected in these materials, even when they are not of more than pliocene age.

3. The ratio of helium to uranium oxide has been measured. This ratio does not strictly follow the order of superposition of the strata; but high ratios are not met with in the younger deposits, whereas they are common in the older ones. It is conjectured that helium has been imperfectly retained, at all events in some cases.

4. Provisional values are given for the time required to accumulate the quantity of helium now found in the nodules and other materials.

In conclusion, I must record my best thanks to Professor Hughes and to Mr. J. J. H. Teall, who have most kindly supplied me with some of the materials used.

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*On Helium in Saline Minerals, and its Probable Connection with Potassium.*

By the Hon. R. J. STRUTT, F.R.S., Professor of Physics in the Imperial College of Science, South Kensington.

(Received July 31, 1908.)

In a former paper\* I mentioned that saline minerals were often comparatively free from contamination with radio-active material of the uranium-radium series. Accordingly they afford special opportunities of testing whether or not helium is generated by the other elements present, namely, sodium, potassium, magnesium, calcium, sulphur, chlorine, oxygen, hydrogen. In this paper determinations are given of helium and radium in some of the saline minerals of Stassfurt. These minerals occur in strata of triassic age, though the age of some of them may be less, for there is evidence that secondary alterations have taken place in the salt deposits.

Helium was liberated by solution of the mineral in water. The powdered substance was placed in a flask fitted up as shown in the preceding paper. The flask was exhausted, washed out with oxygen, again exhausted, and sealed off from the pump. Water, well boiled, and allowed to cool in a vacuum, was admitted through a tap. Heat was applied to promote solution, and when this was complete the gases set free were driven out by boiling and collected over mercury. Carbonic acid was removed by potash, and other constituents by sparking. The small residue was then examined as described in 'Roy. Soc. Proc.,' A, vol. 80, p. 592, liquid air being generally used to cool the charcoal.

When helium had been determined in this way, uranium was determined in the same solution, by the usual method of boiling out the radium emanation generated in a definite period. Previous to this determination the solution was acidified, to dissolve any slight sediment that remained and to prevent precipitation of radium as sulphate.

The results were as follows:—

\* 'Roy. Soc. Proc.,' A, vol. 80, p. 592.

Mineral.	Composition.	Helium, c.mm. per 100 grammes.	Grammes uranium oxide ( $U_3O_8$ ) per 100 grammes.	Helium, c.c. per gramme $U_3O_8$ .
Rock salt .....	NaCl	0·0233	$7·1 \times 10^{-6}$	3·3
Sylvine .....	KCl	0·55*	$2·15 \times 10^{-4}$ †	256
Carnallite.....	$KMgCl_3 \cdot 6H_2O$	0·151*	$3·23 \times 10^{-4}$ †	47
Kieserite .....	$MgSO_4 \cdot H_2O$	0·0179	$6·47 \times 10^{-5}$	0·277

\* These were repeatedly verified. In a specimen of carnallite purchased from another source, helium was scarcely detectible. This may have been due to the specimen having been allowed to deliquesce before it came into my hands. If so, it must have been dried again before I received it.

† In these cases the amount of emanation was too small to be accurately determined. The values given are rough approximations only.

The following were also examined qualitatively :—

Kainite ( $MgSO_4 \cdot KCl \cdot 3H_2O$ ).

Krugite ( $4CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$ ).

Astrakanite ( $Na_2(MgSO_4)_2 \cdot 4H_2O$ ).

Langbeinite ( $K_2SO_4 \cdot 2MgSO_4$ ).

Polyhalite ( $2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 + 2H_2O$ ).

Schœnite ( $K_2Mg(SO_4)_2 \cdot 6H_2O$ ).

Tachyhydrite ( $CaMgCl_6 \cdot 12H_2O$ ).

In none of them was the quantity of helium at all comparable with what was observed in carnallite or sylvine, though  $D_2$  could generally be seen.

Returning to the quantitative experiments it is noticeable that very high ratios of helium to uranium oxide are met with in these two minerals.

It seems altogether improbable that the minute traces of uranium and radium present can account for so much helium. On the other hand, the helium in rock salt is very much of the order to be expected from its geological age, if it originates from the uranium family of radio-active bodies.

In view of Campbell and Wood's observations on the radio-activity of potassium,\* I am disposed to regard that element as the source. It is true that the other potash salts examined do not contain much helium, but, in view of the imperfect retention of the gas in some cases, such negative evidence has not much weight.

The possibility of thorium as a source must not be overlooked. It would be very difficult to determine experimentally whether the small quantity requisite was present; but in view of the freedom of sylvine from more common impurities I think it must be considered unlikely.

\* 'Camb. Phil. Soc. Proc.,' vol. 19, p. 15.



*The Rate of Production of Helium from Radium.*

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S.

(Received August 6, 1908.)

Some time ago I communicated a paper to the Society entitled "Note on the Use of the Radiometer in Observing Small Gas Pressures: Application to the Detection of the Gaseous Products produced by Radio-active Bodies."\* In the course of the experiments recorded in that paper it was shown that a pressure of the fifty millionth of an atmosphere could easily be detected by radiometer motion, and that the helium produced by radio-active processes from some 10 milligrammes of bromide of radium could be definitely detected after a few hours. This led me to desire some direct measurements of the amount of helium produced by radium, and through the kindness of the Royal Society in allowing me the use of some radium chloride belonging to them I am able to give a condensed abstract of the experimental results so far obtained.

The salt employed was the 70 milligrammes of radium chloride prepared by Dr. T. E. Thorpe, F.R.S., for his determination of the atomic weight of radium, the preparation of which is fully described in 'Roy. Soc. Proc.,' A, vol. 80, p. 298.

The apparatus used for the measurements was a McLeod gauge in the construction of which no indiarubber joints were used; the mercury reservoir being connected to an exhaust pump, while the elevation and lowering of the mercury was carried out by admitting and exhausting air in the reservoir. The air coming in contact with the mercury was purified by passage over stick-potash and phosphoric anhydride. Sealed on to the gauge was a long U-tube containing a  $\frac{1}{4}$  gramme of cocoanut charcoal placed in a small enlargement at the bend, the whole being arranged for liquid air or other cooling for any desired length of time. The object of the use of this cooled charcoal is to take up and condense all adventitious gases, other than hydrogen or helium, which might arise from minute leakage or otherwise be generated in the apparatus. The radium chloride was contained in a small bottle standing in a cylindrical glass bulb connected by a T-joint to the U-tube. To the other arm of the T was sealed a bulb containing about 15 grammes of cocoanut charcoal for producing a high exhaustion in the apparatus when cooled to  $-190^{\circ}$  C. The whole apparatus was well exhausted by mechanical

\* 'Roy. Soc. Proc.,' A, vol. 79, p. 529, 1907.

means, all the glass tubes being heated as well as the charcoal receptacles and the radium chloride. On immersing the receptacle containing the 15 grammes charcoal in liquid air for some hours, while the  $\frac{1}{4}$  gramme charcoal and the radium chloride were kept hot, an exhaust of 0.00015 mm. was obtained. This charcoal receptacle was now sealed off and the small  $\frac{1}{4}$  gramme charcoal tube cooled in liquid air. In two hours an exhaust of 0.000054 mm. was reached.

The volume of the gauge and apparatus being approximately 200 c.c., a knowledge of the pressure in the apparatus gives by a simple calculation the actual volume of gas produced measured at atmospheric pressure and the temperature of the laboratory, and thus the rate of production of helium is obtained. This, referred to the weight of radium present, gives the increment in terms of cubic millimetres of gas per gramme of radium per day.

During the first three days the growth of pressure was very small, amounting to about 0.3 cub. mm. per gramme of radium per day. This was, however, practically all produced in the first day. On then heating the radium the pressure was increased to an amount corresponding to an increment of 0.99 cub. mm. The laboratory having to be closed for a fortnight no observations were taken, and as no part of the apparatus was cooled the emanation had free play throughout. About the 350th hour after heating the radium salt the pressure had increased to a value exactly corresponding to the 0.99 cub. mm. increment observed after the first three days. This rate was, however, only kept up for the two succeeding days during which the radium was not heated. On heating the radium a further increase of pressure was obtained (corresponding to a 1.1 cub. mm. increment measured from the start) which largely disappeared on cooling the radium and did not reappear on presently heating the radium again. From this stage throughout the next 120 hours the pressure rapidly became less, despite the heating of the radium, which only temporarily and partially restored it; and after 610 hours a lower pressure was recorded than that obtained immediately after the period of no observations, *i.e.* after 400 hours.

The charcoal was now heated to 450° C. by boiling sulphur. Then on again cooling it with liquid air the pressure was found to have been restored by an amount equal to one-third of that lost as stated above. This, however, quickly disappeared, and apart from fluctuations caused by heating, the radium remained during the next 300 hours at about the value observed just before heating the charcoal to 450° C.

At this point the charcoal was again heated in boiling sulphur and the previous result was repeated. In the ensuing 150 hours, however, the pressure, after falling a little, remained fairly steady, and then showed

a definite and maintained increase for three days, not permanently affected by again heating the charcoal to  $450^{\circ}\text{C}$ .

The quantity of permanent gas produced up to 1100 hours corresponded to an increment of 0.417 cub. mm. per gramme of radium per day taken over the whole period. At this point the radium was sealed off and the first experiment ended.

The large increase over the period in which the charcoal and the radium were both at ordinary temperatures may find some explanation from the unchecked action of the emanation on the charcoal, organic matter and combined moisture possibly present on the walls of the glass tubes of the apparatus, in quantities though small yet large enough to produce the total amount of gas present which, as measured with charcoal at the ordinary temperature, corresponded to a pressure of 1—2 mm.

It may be noted that on the supposition of this gas being largely due to a continuous air leak, the amount of uncondensed gases of the helium type thus introduced would be infinitesimal.

Apart from the possible presence in the apparatus of organic material the radium itself might conceivably at the beginning have been contaminated with traces of organic matter, and a further experiment was decided on to which these objections could not be applied.

In the second experiment the gauge as well as the connecting tubes were well cleaned out with nitric acid and all thoroughly dried. The radium, after the 1100 hours in which it was under high exhaustion and had been frequently heated, was certainly in a more satisfactory condition. Further, to prevent the unchecked action of the emanation throughout the apparatus, the little charcoal condenser was maintained at a degree or two below that of the boiling point of oxygen by the use of old liquid air for a period of about six weeks. A larger quantity of charcoal was used, viz., 1 gramme, the more effectively to condense out extraneous gases while leaving any helium substantially unaffected. This charcoal had been treated with chlorine at a red heat and subsequently with hydrogen.

Beyond this the conduct of the experiment followed the lines of the former one. The mercury pump exhaust was continued for several hours and was carried to 0.002 mm. The large charcoal bulb was then cooled for several hours in liquid air while heating the 1 gramme of charcoal and the radium salt. A pressure as low as 0.00005 mm. was thus obtained when the charcoal was sealed off. On now placing the U-tube containing a small quantity of charcoal in liquid air the pressure registered was 0.000044 mm.

These conditions were maintained for five days, during which a steady

growth of pressure was observed corresponding to an increment of approximately 0.3 cub. mm. per gramme of radium per day. The radium was then heated with a small Bunsen flame as before to a low red heat, when the pressure was increased by about 40 per cent. This increase showed no sign of disappearing, but during the next week a decided but somewhat irregular growth of pressure was recorded. The radium was again heated, when a further increase of pressure was observed. In the succeeding five days it remained steady, only to be again increased on heating the radium. This treatment was repeated in all 10 times at varying intervals during 1100 hours, and in each case the pressure rose on heating and remained fairly steady on standing. All the observations of the second set of experiments are graphically represented in fig. 1. A mean line is drawn through the observations taken with the radium heated, giving a steadily maintained helium increment of approximately 0.37 of a cub. mm. per gramme of radium per day.

In order to ascertain if any helium was occluded in the cooled charcoal and the surrounding glass, the latter was raised to a low red heat while the tube containing the radium chloride was temporarily cooled in liquid air, with the object of condensing out and localising the emanation coming from the heated charcoal and preventing its access to the gauge. The temperature was maintained for an hour, and then the charcoal was allowed to cool and finally replaced in the liquid air. The radium chloride was then allowed to warm up and was heated to near a low red for a short time. After these alternations no increase in pressure was observed, from which it may be inferred that the occlusion of the helium takes place mainly in that part of the apparatus where the radium chloride is situated.

On two occasions the charcoal was cooled in liquid hydrogen, viz., after 165 hours, and again after 650 hours. The proportionate reduction of pressure was the same in both cases, tending to show that the composition or nature of the gas remaining uncondensed by the liquid air remained the same throughout, although steadily increasing in quantity.

In reference to this last point a separate experiment was made in which pure helium under a small tension, produced by heating 0.5 gramme uranite and passing the gas produced over 1 gramme charcoal cooled in liquid air, was subjected to the action of  $\frac{1}{4}$  gramme of clean exhausted charcoal at the temperature of liquid air and liquid hydrogen respectively. The ratio of the two pressures so obtained was in close agreement with that observed in the radium experiment.

A further test of the purity of the gas producing the permanent pressure observed in the radium experiment with the charcoal cooled in liquid air was made by simply cooling the bulb containing the radium in liquid



hydrogen, allowing the charcoal meanwhile to warm up to  $0^{\circ}$  C. If any hydrogen was present in the gas it is certain that there would be an increase of pressure recorded, since although hydrogen is partially absorbed by charcoal in liquid air yet it would not be reduced in pressure by cooling in liquid hydrogen. On allowing the charcoal therefore to warm up, any hydrogen expelled would remain and cause an increased pressure. Inasmuch as an increase was not recorded, it can be safely assumed that no hydrogen is present, and thus the gas pressure measured consists entirely of helium.

A confirmation of this was made spectroscopically as follows:—Two tin-foil electrodes were placed round the narrow capillary measuring tube of the gauge, near the closed end. These were about 3 cm. long and about  $1\frac{1}{2}$  cm. apart and were wired on with thin copper wire. The gas was compressed into this capillary space, as in taking an ordinary measure to any pressure of the order of 2 or 3 mm., while an induction discharge passed in the gas. The spectroscopic examination of this discharge revealed only the six principal helium lines, mercury, and a trace of the carbonic oxide spectrum. I have shown that the carbonic oxide spectrum always occurs in electrode-less tubes.\*

I am not aware of any previous direct measurements of the rate of production of helium from radium, but in a paper on "Some Properties of Radium Emanation," by A. J. Cameron and Sir William Ramsay,† the ratio of the amount of helium produced to that of the emanation was found to be 3·18, and as the amount of the emanation found by them was about 1 cub. mm. per gramme of radium per day, the resulting helium according to this experiment ought to reach about 3 cub. mm. or at least eight times the rate of production found in the above experiments. I am at a loss to explain the origin of such grave discrepancies in the measured amount of the helium produced by radium.‡ On the other hand, Professor Rutherford, in his work entitled 'Radio-active Transformations,' 1906, p. 186, on the theoretical assumption that the  $\alpha$ -particle is an atom of helium carrying twice the ionic charge, deduced from electrical measurements that the number of particles expelled per year per gramme of radium would reach  $4 \times 10^{18}$ , and as 1 c.c. of a gas at standard temperature and pressure contains  $3\cdot6 \times 10^{19}$  molecules, the volume of helium produced per year would amount to 0·11 c.c., which

\* See paper ('Roy. Soc. Proc.' vol. 64, p. 237) "On the Application of Liquid Hydrogen to the Production of High Vacua; together with their Spectroscopic Examination."

† 'Chem. Soc. Jour.' 1907, p. 1274.

‡ Professor Rutherford, in a paper, "Experiments with Radium Emanation," 'Phil. Mag.', July, 1908, shows this result is at least ten times too great, his value being of the order 0·11 cub. mm. of emanation per day, whereas from my experiments the rate of helium production is just three times this amount.

is equivalent to about 0.3 of a cub. mm. per day. Considering I have found a rate of helium production of the order of 0.37 cub. mm., the agreement between experiment and the theoretical prophecy of Rutherford is almost too wonderful, substantiating as it does the accuracy of the theory of radio-active changes he has done so much to initiate and develop.

I have to express my obligations to Mr. Robert Lennox, F.C.S., and Mr. W. J. Green, B.Sc., for aid given in the conduct of these long and laborious experiments.

*On the Reflection of Waves from a Stratum of Gradually Varying Properties, with Application to Sound.*

By J. W. NICHOLSON, D.Sc., B.A., Isaac Newton Student, Scholar of Trinity College, Cambridge.

(Communicated by Professor J. Larmor, Sec. R.S. Received June 11,—Read June 25, 1908.)

In a variable medium, the velocity of propagation of a train of waves, and the wave-length at any point, are functions of the position of that point. The circumstances of such a propagation have only been worked out in detail in one particular case. Lord Rayleigh,\* in connection with the transverse vibrations of a string of variable density, dealt very completely with the case in which the density is inversely proportional to the distance from a fixed point. In his original investigation† the results were applied to the corresponding optical problem, and a numerical example given.

Although this is perhaps the only interesting case in which a simple exact solution appears possible, yet a close approximation may be made to the existing conditions, even in the general problem, when the waves are short in comparison with the other distances concerned. The development of such a theory, with an examination of some important cases, is the object of the present paper.

Let  $V_0$  be the velocity of a plane wave-train at some point of a medium, which we may choose as origin, and suppose that the train is advancing along the direction  $x$ .

\* 'Theory of Sound,' vol. 1, § 148.

† 'Proc. Lond. Math. Soc.,' vol. 11, 1880, pp. 51—56; 'Collected Papers,' vol. 1, pp. 460—465.

The velocity  $V$  at the point defined by  $x$  is taken as a function of  $x$  only. In order that the results may not be restricted to any particular class of vibrations, let  $\phi$  be the vector, of whatever character, whose propagation defines the vibration.

In all important cases,  $\phi$  may be chosen such a vector that the surface conditions are

- (i)  $\phi$  is continuous,
- (ii)  $d\phi/dx$  is continuous.

The equation of propagation  $\frac{d^2\phi}{dt^2} = V^2 \frac{d^2\phi}{dx^2}$  yields for a simple wave-train

$$d^2\phi/dx^2 + k^2\phi = 0, \quad (1)$$

where  $2\pi/k$  is the wave-length  $\lambda$ , which is a function of  $x$ .

If  $k_0$  is the value of  $k$  at the origin, we may assume a relation

$$k = k_0 f(x). \quad (2)$$

When  $k_0$  is preponderant over  $f(x)$ , the approximate solution of the differential equation may be obtained by a method described by H. A. Webb,\* after Horn, but employed earlier as a working method by Stokes† and L. Lorenz.‡

Write 
$$\phi = e^{\pm i k_0 \omega} \psi, \quad (3)$$

where  $\omega$  and  $\psi$  are functions of  $x$  to be suitably chosen. If accents denote differentiations with respect to  $x$ , we obtain

$$\psi'' \pm i k_0 (\psi \omega'' + 2\psi' \omega') - k_0^2 \psi (\omega'^2 - f^2(x)) = 0.$$

Equating the coefficients of  $k_0$  and  $k_0^2$  separately to zero, since the terms are of different orders of magnitude, we obtain, if  $A$  is an arbitrary constant, and if the first term proves negligible, as will appear in the cases treated,

$$\omega = \int^x \sqrt{f(x)} dx, \quad \psi = A/\sqrt{\omega'}. \quad (4)$$

Thus the general solution, when the variable part of  $k_0 \omega$  is small compared with  $k_0$ , of the equation

$$\partial^2 \phi / \partial x^2 + k_0^2 \omega'^2 \phi = 0, \quad (5)$$

where  $\omega'$  represents  $\partial \omega / \partial x$ , is obtained in the form

$$\phi = (A e^{i k_0 \omega} + B e^{-i k_0 \omega}) / \omega'^{1/2}. \quad (6)$$

We proceed to discuss the reflection backward of waves travelling along  $x$ , in traversing a medium of this slowly changing character, and of extent large compared with the wave-length. Let the medium be uniform from

\* 'Roy. Soc. Proc.' vol. 74, 1904, p. 315.

† 'Math. and Phys. Papers,' vol. 2, p. 334.

‡ 'Œuvres Scientifiques,' vol. 1, p. 435 *et seq.*



$x = -\infty$  to  $x = x_1$ , slowly variable from  $x = x_1$  to  $x = x_2$ , and again uniform, but differently so, from  $x = x_2$  to  $x = \infty$ , there being perfect material continuity at  $x_1$  and  $x_2$ , and the values of  $\omega$  in the extreme media being  $\omega_1$  and  $\omega_2$ .

A wave advancing along  $x$  positive into the varying stratum is of type

$$\phi_1 = H e^{-i k_0 \omega_1' (x-x_1)}, \quad (7)$$

to which corresponds a reflected wave, emerging from it,

$$\phi_2 = K e^{i k_0 \omega_1' (x-x_1)}. \quad (8)$$

The time factor, say  $e^{ict}$ , is included in  $H$  and  $K$ .

In the intermediate variable stratum, the complete direct and reflected disturbance is given by (6), and in the final uniform medium, where there can be no negative wave,

$$\phi = C e^{-i k_0 \omega_2' (x-x_1)}. \quad (9)$$

If  $\mu_{12}$  is the refractive index between the terminal media in the optical case, then  $\mu_{12} = \omega_2' / \omega_1'$ .

The surface conditions at  $x = x_0$ ,  $x = x_1$  lead to

$$(H + K) \omega_1'^{\frac{1}{2}} = A e^{i k_0 \omega_1} + B e^{-i k_0 \omega_1},$$

$$C \omega_2'^{\frac{1}{2}} = A e^{i k_0 \omega_2} + B e^{-i k_0 \omega_2}$$

$$-i k_0 (H - K) \omega_1'^{\frac{1}{2}} = A e^{i k_0 \omega_1} (\omega_1'' - \omega_1' / 2 \omega_1'^2) - B e^{-i k_0 \omega_1} (\omega_1'' + \omega_1' / 2 \omega_1'^2),$$

$$-i k_0 C \omega_2'^{\frac{1}{2}} = A e^{i k_0 \omega_2} (\omega_2'' - \omega_2' / 2 \omega_2'^2) - B e^{-i k_0 \omega_2} (\omega_2'' + \omega_2' / 2 \omega_2'^2).$$

$$\text{If } s = e^{i k_0 (\omega_2 - \omega_1)}, \quad 2i k_0 (\epsilon_1, \epsilon_2) = (\omega_1'' / \omega_1'^2, \omega_2'' / \omega_2'^2),$$

where  $(\epsilon_1, \epsilon_2)$  are small pure imaginaries of the order of a wave-length, then

$$H \begin{vmatrix} 2 - \epsilon_1 & -\epsilon_1 & 0 \\ s & s^{-1} & 1 \\ s(1 - \epsilon_2) & -s^{-1}(1 + \epsilon_2) & -1 \end{vmatrix} = K \begin{vmatrix} \epsilon_1 & 2 + \epsilon_1 & 0 \\ s & s^{-1} & 1 \\ s(1 - \epsilon_2) & -s^{-1}(1 + \epsilon_2) & -1 \end{vmatrix}$$

$$\text{Thus } K/H = \{\epsilon_2(2 - \epsilon_1) - s^2 \epsilon_1(2 - \epsilon_2)\} / \{\epsilon_1 \epsilon_2 + s^2(2 + \epsilon_1)(2 - \epsilon_2)\}, \quad (10)$$

which determines the amplitude and phase of the reflected wave.

At present we consider only the case in which  $\omega_1$  and  $\omega_2$  are real. The square of the wave-length being small compared with that of the distance traversed, as required for this analysis, the result takes a simpler form.

$$\begin{aligned} \text{Write } \omega_2 - \omega_1 &= \beta, & 2k_0(\epsilon_1, \epsilon_2) &= i(\alpha_1, \alpha_2), \\ \text{so that } \alpha &= -\omega'' / \omega'^2, \end{aligned} \quad (11)$$

and is purely real. Then

$$\begin{aligned} K/H &= (\epsilon_2 - \epsilon_1 \exp 2i k_0 \beta) / 2 \exp 2i k_0 \beta \\ &= (\alpha_2 \sin 2k_0 \beta - i \alpha_1 + i \alpha_2 \cos 2k_0 \beta) / 4k_0. \end{aligned}$$

If  $R$  is the ratio of the intensities of the reflected and incident waves,

$$R = (\alpha_1^2 + \alpha_2^2 - 2\alpha_1 \alpha_2 \cos 2k_0 \beta) / 16k_0^2; \quad (12)$$

also the increase of phase in the reflection, measured at the front  $x_1$ , is  $\theta$ , where

$$\tan \theta = (\alpha_2 \cos 2k_0\beta - \alpha_1) / \alpha_2 \sin 2k_0\beta. \quad (13)$$

Higher approximations may be found if desired; the value of the function  $\psi$  previously used may be found to a higher order by writing, in the equation of propagation,

$$\phi = e^{ik_0\omega} \left( \psi_1 + \frac{\psi_2}{k_0} + \frac{\psi_3}{k_0^2} + \dots \right). \quad (14)$$

*Verification of the Approximation.*

The result may be tested by comparison with Lord Rayleigh's solution for a particular case previously referred to, which is mathematically exact.

In that case  $\omega' = x^{-1}$ ,  $\alpha = -\omega''/\omega'^2 = 1$ ,

$$\beta = \omega_2 - \omega_1 = \log x_2/x_1 = \log \mu,$$

where  $\mu$  is the refractive index between the extreme media, which is to be not much different from unity.

$$\text{Thus} \quad I = \sin^2(k_0 \log \mu) / 4k_0^2, \quad (15)$$

while Lord Rayleigh's result is

$$I = \sin^2(k_0 \log \mu) / \{4k_0^2 + \sin^2(k_0 \log \mu)\},$$

so that the agreement is close even for only moderately large values of  $k_0$ .

*Effect of an Absorbing Medium.*

If the second medium have an absorbent effect, the differential equation relating to it has a term proportional to the velocity, and becomes

$$\partial^2 \phi / \partial t^2 + \sigma \partial \phi / \partial t = V^2 \partial^2 \phi / \partial x^2, \quad (16)$$

where  $V$  is the velocity of propagation, and  $\sigma$  is a certain constant whose value must be positive. A negative value would denote instability of the medium.\*

If  $\phi$  has a time factor  $e^{ict}$ , and  $2\pi/k$  is the wave-length at the origin as before,

$$\partial^2 \phi / \partial x^2 + (k^2 - iC\sigma) \phi = 0, \quad (17)$$

and absorption may be accounted for by taking the function  $\omega$  as complex. But the imaginary portion must be essentially negative.

If, therefore, the second medium be absorbent,  $\epsilon_2$ , and therefore  $\beta$ , is complex, and we may write

$$\beta = \lambda - i\mu,$$

where  $\lambda$  and  $\mu$  are positive.

\* Cf. a discussion by Lord Rayleigh, of Cauchy's "Theory of Reflection by Opaque Bodies," 'Phil. Mag.' vol. 42, 1871, p. 441; 'Collected Works,' vol. 1, p. 145.

Thus, in previous notation,

$$\begin{aligned} K/H &= (\epsilon_2 - \epsilon_1 \exp 2ik_0\beta)/2 \exp 2ik_0\beta \\ &= (\epsilon_2 - \epsilon_1 \exp 2k_0\mu \exp 2ik_0\lambda)/2 \exp 2k_0\mu \exp 2ik_0\lambda. \end{aligned}$$

Even when  $\mu$  is fairly small the function  $\exp 2k_0\mu$  may be very large, if the wave-length be small enough, and approximately, in this case,

$$K/H = -\frac{1}{2}\epsilon_1 = i\alpha_1/4k_0.$$

The ratio of the intensities of the reflected and incident waves becomes

$$R = \alpha_1^2/16K_0^2. \quad (18)$$

A very moderate amount of absorption is sufficient, in these circumstances, to render the reflected wave practically independent of it, and to destroy entirely the periodic effects with changing thickness of layer, which obtain in the absence of absorption. The value of  $R$  in (18) may be called the "limiting" intensity.

In order to obtain a general idea of the validity of this reasoning, it is sufficient to consider the special case of linear variation of the medium, which will usually occur in practice. The amount of variation in the medium, of which this analysis can take account, must first be estimated.

In obtaining (4),  $\psi''$  was neglected, where  $\psi$  then became  $A/\sqrt{\omega'}$ .

The ratio borne to  $\psi''$  by the greatest term retained in the differential equation is of order

$$k_0\psi\omega''/\psi'' = k_0\omega''\omega^{-\frac{1}{2}}/(\frac{1}{2}\omega''/\omega^{\frac{1}{2}} + \dots);$$

and for a law of variation given by

$$\omega' = 1 + cx,$$

where  $x$  is distance from the origin 0, this becomes

$$4k_0\omega'(1+cx)/3c, \text{ or } 8/c\lambda$$

practically, on reduction, where  $\lambda$  is the "mean" wave-length.

Thus if  $c$  is so great that  $c\lambda = \frac{1}{2}$ , the error involved is not greater than about 6 per cent. This may be taken as an extreme case in which the analysis is approximately correct.

If  $c$  is entirely due to absorption, it may be written  $-i\mu$ , where  $\mu$  is real and positive, and  $2\mu\lambda$  may be as great as unity. Thus  $\omega' = 1 - i\mu x$ ,

$$[\omega]_1^2 = [x - \frac{1}{2}i\mu x^2]_1^2 = \beta,$$

and if  $d$  is the thickness of the stratum,  $\exp 2ik_0\beta$  contains a factor  $\exp \mu k_0 d^2$ , whose value is approximately  $\exp (3d^2/\lambda^2)$  in the extreme case  $2c\lambda = 1$ , where  $\lambda$  is again the "mean" wave-length. This quantity is very large even if  $d$  is but a wave-length. The result obtained for the general case is therefore justified under these circumstances.

The formula for the transmitted wave discussed below indicates that in a case like the present the intensity of that wave contains a factor  $\exp(-2ik_0\beta)$ , or  $\exp(-3d^2/\lambda^2)$  when the absorption is extreme. It therefore appears that the disappearance of the periodic effect with varying thickness of layer corresponds, in general, to an absorption which is very complete in less than a wave-length.

The analysis has been shown capable of taking account of this small thickness of stratum, provided the rate of change be not too rapid. For any wave-length there is a limiting amount of change to which the method applies, given by  $2c\lambda = 1$  within an error of 6 per cent. A greater absorption requires a smaller mean wave-length.

### *The Transmitted Wave.*

In the more general case with previous notation, it may be readily shown that

$$C/H = 4s(\omega_1'/\omega_2')^{1/2} / \{\epsilon_1\epsilon_2 + s^2(2 + \epsilon_1)(2 - \epsilon_2)\}, \quad (19)$$

which determines the amplitude and phase of the transmitted wave.

When  $\epsilon_2$  is real, we may neglect  $\epsilon_1$ ,  $\epsilon_2$ , and also  $\epsilon_1\epsilon_2$  in comparison with unity.

Thus

$$C/H = 1/s\sqrt{\mu_{12}},$$

and the incident wave,  $\phi = H \cos \{k_0\omega_1'(x-x_1) - Vt\}$ , leads to a transmitted undulation,

$$\phi_2 = H\mu_{12}^{-1/2} \cos \{k_0\omega_2'(x-x_1) + k_0(\omega_2 - \omega_1) - Vt\}. \quad (20)$$

When  $\beta$  is complex of the form  $\lambda - i\mu$ , and  $\mu$  is positive,  $s$  contains a factor,  $\exp - k_0\mu$ , making it very small. Since this expression in the numerator of (19) will completely outweigh the smallness of the denominator, there is no appreciable transmitted wave. It is, in fact, wholly absorbed, in accordance with the character then possessed by the second medium.

### *Discussion of the Results.*

Reverting to the case in which  $\omega_2$  is real, to which corresponds the formula (12), we note that the intensity of reflection, for increasing thickness of the layer, has maxima and minima after the manner of Newton's rings in optics. But since  $\alpha_1^2 + \alpha_2^2 - 2\alpha_1\alpha_2$  is essentially positive, absolute extinction of the reflected waves is only possible when this quantity is zero, and therefore when  $\alpha_1 = \alpha_2$ .

The possible laws of slow variation to enable this to happen apart from those of periodic character are contained in  $\omega''/\omega'^2$  constant or

$$\omega' = a/(bx+c), \quad (21)$$

which leads only to the case discussed by Lord Rayleigh. For all other laws, maxima and minima of reflection occur as the thickness of the layer varies.

The change of phase in (13) is measured at the plane  $x = x_1$ , where the waves enter the second medium. If the phase is unaltered, except by reversal,

$$\alpha_2 \cos 2k_0\beta = \alpha_1,$$

whence

$$\cos 2k_0\beta = \mu_2^2 \left( \frac{d\mu}{dx} \right)_1 / \mu_1^2 \left( \frac{d\mu}{dx} \right)_2,$$

on putting  $\omega' = C\mu$ , where  $C$  is constant and  $\mu$  is the index of refraction at a point. This equation can be satisfied by real values if

$$\frac{d}{dx_2} \left( \frac{1}{\mu_2} \right) \text{ does not exceed } \frac{d}{dx_1} \left( \frac{1}{\mu_1} \right). \quad (22)$$

When limiting reflection is attained, owing to complete but very gradual absorption in the second slightly different medium, the change of phase must be  $\frac{1}{2}\pi$ . This is a case in which absorption takes place almost entirely in a wave-length.

#### *Reflection of Sound from a Fog.*

The results have some bearing upon the question of the action of a fog upon incident sound waves. The observations of Tyndall\* and Henry† showed that sounds of different pitches vary their order of effectiveness, at a distance, in a remarkable manner. Henry made certain conjectures as to the motion of the air overhead, and regarded the consequent refraction‡ as the agent causing the peculiarities shown by distant sounds. Tyndall, however, whose view seems to be in accordance with many of the observations on fog-signals, postulated the existence of a flocculent condition of the atmosphere in such cases, caused by unequal heating, or by the presence of an excess of moisture in certain parts. The views of Stokes and Henry have been developed independently by Osborne Reynolds,§ who points out that, since wind raises sound by causing it to move faster below than above, any other cause producing such a difference in velocity of propagation must also lift the sound. Such a cause is the temperature gradient in the atmosphere. Adopting the results of Glaisher's balloon observations,|| Reynolds has calculated that the range of Tyndall's sounds might at any time have been extended by a quarter of a mile, had he been able to ascend 30 feet.

\* 'Phil. Trans.,' vol. 164 1874, p. 183.

† 'Report of the U.S. Naval Board for 1874.'

‡ Stokes, 'Math. and Phys. Papers,' vol. 4, p. 110.

§ 'Roy. Soc. Proc.,' vol. 22, 1874, p. 296.

|| 'Brit. Ass. Report,' 1862, p. 462.

Although Reynolds has pointed out that some of Tyndall's own observations may be explained by refraction, yet Lord Rayleigh\* has cited others which appear explicable only by acoustic clouds. Moreover, the explanation by refraction of the increase in the range of sound when the sky becomes cloudy, or when evening approaches, appears to admit of an alternative. An atmosphere with much aqueous vapour present has a greatly increased power of radiating, as well as of absorbing heat, and the removal of the sun's effect might therefore produce the acoustic phenomenon in question.

The formulæ given above allow an estimate of the efficiency of the cause assigned by Tyndall. A portion of the numerator of the expression (12) obtained for the reflected intensity is periodic, and depends both upon the period of the sound and the degree of heterogeneity of the medium. For the present we are neglecting the small radiation of heat which takes place during the passage of sound. A slight change in  $k_0$  does not appreciably modify the denominator of (12), but can cause a great alteration in the numerator: and sounds whose periods are not far apart can thus exhibit, under certain circumstances, a fair amount of difference in effectiveness. This is in accordance with observations. Since, moreover,  $k_0$  is large compared with the varying part of  $\beta$ , a fairly small amount of variation of the medium, not greatly changing  $\alpha_1$  and  $\alpha_2$ , may cause a more considerable change in  $k_0\beta$  which may suffice to change the order of effectiveness of two sounds. A moderately small change in  $\beta$  may cause  $\sin 2k_0\beta$  to oscillate between the limits  $\pm 1$ , so that the corresponding intensity of reflected sound oscillates between the limits

$$(\alpha_1 \pm \alpha_2)^2 / 16k_0^2, \quad (23)$$

which may differ fairly widely.

This line of reasoning seems capable of explaining many of the vagaries of sounds coming from a distance. In foggy weather the atmosphere is more homogeneous than usual, and the backward reflection is extremely small. The sounds then have little tendency to vary their order of effectiveness, and signals are also effective at much greater distances than ordinarily.

Tyndall's "acoustic clouds" were regarded by him as being mainly due to the presence of an excess of aqueous vapour in some parts of the atmosphere. Now, moist air has a greater power of radiating heat than dry air, and the consequent "stifling" of the sound passing through very moist air† may be appreciable, although in air under ordinary conditions the effect is negligible. Tyndall does not give a definite idea of the nature of the action of an acoustic cloud, which may act, for the purposes of his theory, by stifling the

\* 'Theory of Sound,' 1896, § 290.

† Stokes, 'Phil. Mag.,' April, 1851; 'Math. and Phys. Papers,' vol. 3, p. 142.

sound, by scattering, or by reflecting it back to its starting point. Probably the first two effects both play their proper parts. Moreover, as we have shown, the backward reflection when sound enters such a dissipative medium tends to lose its periodicity, and to be independent of the reflecting medium when the dissipation exceeds a certain limit.

The theory of Stokes shows that the  $k^2$  of the ordinary equation of wave motion is to be replaced by  $k^2\gamma(q + in)/(q + i\gamma n)$ , where  $2\pi/n$  is the period of the sound, and  $q$  is the radiation constant.\*

Since  $q$  is small compared with  $n$ , as proved by Stokes, and  $\gamma = 1.4$ , it appears that  $k_0\omega'$  is to be replaced by

$$k_0\omega'(1 - iq/7n).$$

As a limiting case, we will suppose that  $q$  is zero in air, and that the variable medium of the preceding theory is the layer of transition between ordinary air and an acoustic cloud.

Assuming the transition to take place uniformly, we may replace  $q$  by one-half its final value. Thus,  $k_0(\omega_2 - \omega_1)$  is to be replaced by  $k_0(\omega_2 - \omega_1)(1 - iq/14n)$ . Now, the general effect of such a complex value of  $\beta$  has been already seen to be a tendency towards a certain "limiting" reflection of the sound.

The value of the quantity  $\exp 2ik_0\beta$ , when  $q$  is present, bears to the value, when  $q$  is zero, the approximate ratio  $\exp \frac{1}{2}k_0(\omega_2 - \omega_1)q/n$ .

In considering the effect of  $q$  apart from that of the variation of wavelength, which is itself small, we may write  $k_0(\omega_2 - \omega_1) = k(x_2 - x_1)$ . The argument of the above exponential therefore becomes  $q(x_2 - x_1)/7V$ . If this have a value of about 5 only, there is a reflection which is almost limiting, since  $e^5$  is about 144, a value sufficiently great in general for the above theory of limiting or non-periodic reflection to apply. In the absence of any evidence† that  $q$  is inappreciable for a cloud composed largely of vapour, it appears possible that an acoustic cloud may act in this manner, if the layer of transition have a length  $(x_2 - x_1)$  sufficiently great.

In this case, all the phenomena noticed by Tyndall would seem capable of explanation by his theory. The order of effectiveness of sounds noticed on a day during which the atmosphere is uniform may change when acoustic clouds arise. For when they are present, the maxima and minima depending on the formula (12) may cease to be found.

Lord Rayleigh has pointed out that the presence of an acoustic fog would probably not influence a sound of very short duration, such as the report of

\* Cf. Lord Rayleigh, 'Theory of Sound,' vol. 2.

† Vide the Appendix.

a gun, in the same manner as the prolonged sound given out by a siren. Moreover, the diffraction round obstacles may be less effective for sounds of short duration. These effects of the *duration* of the sound are, however, independent of the considerations treated at present.

*Upward Propagation of Sound in the Atmosphere.*

The presence in the atmosphere of a temperature gradient, and of a variation of density due to gravity, each cause the circumstances of propagation of sound to vary with the height. When sound travels upward, each will cause a certain fraction to be reflected back to the earth. We may consider the effects separately, since both are small, and will first treat that of the temperature gradient.

Let  $V$  be the velocity at a height  $z$ , and  $V_0$  that at the earth. If  $(p, \rho)$ ,  $(p_0, \rho_0)$  are the corresponding pressures and densities, then in convective equilibrium

$$p\rho^\gamma = \text{constant},$$

and

$$V^2 = dp/d\rho = \gamma p_0 \rho^{\gamma-1} / \rho_0^\gamma.$$

Since

$$dp = -g\rho dz,$$

we deduce

$$V^2 = V_0^2 - (\gamma - 1)gz. \quad (24)$$

If  $2\pi/p$  is the period of the sound,

$$k_0 = p/V_0,$$

and

$$\omega' = (1 - \epsilon z)^{-\frac{1}{2}}, \quad \alpha = -\frac{1}{2}\epsilon\omega', \quad \omega\epsilon = -2(1 - \epsilon z)^{\frac{1}{2}},$$

where

$$\epsilon = (\gamma - 1)g/V_0^2.$$

Hence, since  $\omega' = 1$  at the surface,  $z = 0$ , the intensity ratio of the sound reflected from the stratum of height  $z$ , by the formula (12), becomes

$$R = \left\{ 1 + (1 - \epsilon z)^{-1} - 2(1 - \epsilon z)^{-\frac{1}{2}} \cos \frac{4p}{V_0\epsilon} (1 - (1 - \epsilon z)^{\frac{1}{2}}) \right\} \frac{\epsilon^2 V_0^2}{64p^2}.$$

Since  $\epsilon$  is very small, we may write, retaining only its lowest powers,

$$R = \frac{(\gamma - 1)^2 g^2}{16p^2 V_0^2} \left\{ 1 + \frac{(\gamma - 1)gz}{2V_0^2} \right\} \sin^2 \frac{pz}{V_0}. \quad (25)$$

If  $\lambda_0$  is the wave-length at the surface of the earth, there is extinction of reflected sound when

$$2\pi z/\lambda_0 = s\pi \quad \text{or} \quad z = \frac{1}{2}s\lambda_0, \quad (26)$$

where  $s$  is an integer.

For air under ordinary conditions we may write

$$\gamma = 1.41, \quad g = 32, \quad V_0 = 1100 \text{ feet per second, and } p = 2\pi V_0/\lambda_0,$$



whence we obtain

$$R = 13 \cdot 10^{-15} \lambda_0^2 \{1 + 21 \cdot 10^{-7} z\} \sin^2 2\pi z / \lambda_0, \quad (27)$$

where  $z$  and  $\lambda_0$  are measured in feet.

The total reflection due to the temperature gradient is thus very small, and is a periodic function of  $z$  whose amplitude increases very slowly with  $z$  in a linear manner. This discussion of the case of convective equilibrium gives a general idea of the order of magnitude and mode of variation of the effect for other distributions of temperature in the atmosphere.

*Effect of the Gradient of Atmospheric Density on Upward Propagation.*

With the usual notation, if  $z$  be measured upwards, the equation of upward propagation of sound in the atmosphere is

$$\rho \frac{\partial^2 u}{\partial t^2} = -\frac{\partial p}{\partial x},$$

where  $u$  is displacement, and, by Boyle's law,

$$p / \rho \tau = p_0 (1 + \partial u / \partial x) / \rho_0 \tau_0.$$

Thus 
$$\rho \frac{\partial^2 u}{\partial t^2} = V_0^2 \frac{\partial}{\partial x} \left( \rho \frac{\partial u}{\partial x} \right). \quad (28)$$

If  $2\pi/k_0$  is the wave-length at the surface of the earth, where the velocity is  $V_0$ , then

$$\frac{\partial}{\partial x} \left( \rho \frac{\partial u}{\partial x} \right) + k_0^2 \rho u = 0,$$

or 
$$\frac{\partial^2 u}{\partial y^2} + k_0^2 \rho^2 u = 0, \quad (29)$$

where 
$$y = \int^x dx / \rho. \quad (30)$$

The  $\omega'$  of the formula (6) is now  $\rho$  and the  $\omega$  is  $\int^y \rho dy$  or  $x$ . Moreover,

$$\omega'' = \partial \rho / \partial y = \rho \partial \rho / \partial x = \rho \rho'.$$

Thus 
$$\alpha = -\omega'' / \omega'^2 = -\rho' / \rho.$$

But 
$$\log \rho_0 / \rho = gx / k,$$

where  $k$  is the compressibility.

Thus 
$$\alpha_1 = \alpha_2 g / k,$$

and therefore by the formula (12) the intensity ratio of sound reflected from a height  $x$  is

$$R = g^2 \sin^2 \cdot k_0 \beta / 4 k_0^2 k^2. \quad (31)$$

For air under ordinary conditions,  $g = 32$ ,  $k = (1100)^2 / 1.41$ .\*

\*  $g/k$  is so small that this result holds even for very small heights, examining  $\psi''$  of (4).

forming the calculation, it appears that for sound whose wave-length, expressed in feet, is  $\lambda$ ,

$$R = 8.7 \cdot 10^{-12} \cdot \lambda^2 \sin^2 2\pi z / \lambda. \quad (32)$$

This effect is of the same character as that of the temperature gradient. For a given height, the effect of the variation of density is about 700 times as great as that of the temperature variation, provided that the ratio of height to wave-length is great.

The type of analysis here employed is applicable to many other physical problems connected with short waves, such, for example, as that of short waves of transverse displacement in an infinite stretched string.

APPENDIX.—*On Viscosity, Radiation, and Conduction, and their Effect on the Propagation of Sound in a Variable Medium.*

This appendix is an amplification of the previous discussion of stifling by moist air. It was there tacitly assumed that dissipation of sound took place merely by radiation of heat during its passage. This was based on the fact (*infra*) that radiation is the factor most liable to cause appreciable dissipation in sounds of any pitch whatever.

Other factors capable of causing it for a smaller range of pitch are viscosity and conduction.

If  $\mu$  is the kinematic viscosity, and  $\nu$  the thermometric conductivity, then the equation of propagation of sound, when these dissipative agencies alone act, is\*

$$u = e^{-mx} \cdot \cos (nt - x/V),$$

where

$$m = \frac{n^2}{2V^3} \left( \frac{4}{3} \mu + \frac{\gamma - 1}{\gamma} \cdot \nu \right).$$

In C.G.S. units  $\mu = 1.4$ ,  $\nu = 0.26$ ,†

and thus  $m = 0.12 n^2 / V^3$ .

Now  $V = 33,200$  cm. per second, and for a sound of frequency  $n/2\pi = 256$ ,  $m = 1.02 \cdot 10^{-8}$  cm.<sup>-1</sup>.

It was shown above that the quantity  $\exp 2ik_0\beta$  of reflected sound in a variable medium, when radiation is present, bears to that when radiation is absent the ratio

$$\exp \frac{1}{2} q (x_2 - x_1) / V, \text{ or } \exp m_1 (x_2 - x_1).$$

Here  $m_1$  is the quantity in the dissipation ratio  $e^{-m_1 x}$  due to radiation alone, which occurs in ordinary propagation in a uniform medium.

\* Kirchhoff, 'Pogg. Ann.,' vol. 134, p. 177, 1868; Lord Rayleigh, 'Theory of Sound, 2nd edition, § 348.

† E. Müller, 'Wied. Ann.,' vol. 60, p. 113, 1896.

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Thus  $m_1 = q/7V = 0.44 \cdot 10^{-8} q \text{ cm.}^{-1}$ ,  
and  $m_1/m = 436q$ .

Thus if  $q$  be not less than about  $1/500$ , radiation is the predominant factor in dissipation of sounds of low pitch, and, therefore, also in causing limiting reflection when the medium is not uniform.

For a sound of very high pitch, radiation is not so necessarily predominant. In the case of a sound of frequency 5000,  $m_1/m = q$  (approx.).

As to the value of  $q$ , much divergence of opinion exists. Wilmer Duff,\* in a series of experiments on the rate of fall of intensity of sounds of frequency about 7000, concluded that the great rate he obtained could only be explained by assigning to  $q$  a value 8.3 in ordinary air. Apparently valid reasons were given for supposing that atmospheric refraction and internal reflection had not played any appreciable part in affecting the rate of fall, for the conditions of the atmosphere and the circumstances of position appear to have varied widely. Moreover, wind was almost absent, and the vertical temperature gradient, the other chief cause of refraction, must have been subject to variation, as observations were taken both at noon and after sunset.

But Lord Rayleigh,† in examining these results, concluded that the radiating power must be hundreds of times smaller, and attributed Duff's results to atmospheric refraction, or to some hitherto neglected cause. He suggested, as a possible cause, a delay in the equalisation of different kinds of energy in a compressed gas not insensible in comparison with a period of sound, and thus causing dissipation. This criticism was supported by an argument based on the theory of exchanges, and by an experiment on the lines of that used by Clement and Desormes in determining  $\gamma$ . The agreement of this experiment with corresponding theory‡ appears to be conclusive, and we must therefore suppose that  $q$  is not of order unity for ordinary air. This justifies the assumption made in a previous portion of this paper that  $q = 0$  for ordinary air. But for very moist air the value of  $q$  does not appear to have been examined experimentally, and we have no indirect knowledge of it, except that it is greater than in ordinary air. That its value may be considerable in comparison with that for dry air seems fairly certain. Moreover, the viscosity  $\mu$  and conductivity  $\nu$  may be, and probably are, considerably greater in moist air, thus lending support to the argument based on (18), by adding their effects to those of  $q$  (which latter probably predominates, except for sounds of very high pitch).

\* 'Physical Review,' March, 1898.

† 'Phil. Mag.,' vol. 47, p. 308, 1899.

‡ 'Phil. Mag.,' vol. 47, p. 314, 1899.

Until the values of these quantities ( $\mu$ ,  $\nu$ ,  $q$ ), and more especially of  $q$ , are known for very moist air, the explanation given by Tyndall of his own observations must be regarded as a very possible one, for the change of character of the reflection effect of (12) may readily occur in a sufficiently large layer, if the three coefficients ( $\mu$ ,  $\nu$ ,  $q$ ) be at all appreciably modified by the presence of moisture. We may note that the effect of  $q$  alone is independent of the pitch.

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*On the Nature of the Streamers in the Electric Spark.*

By S. R. MILNER, D.Sc. (Lond.), Lecturer in Physics, the University of Sheffield.

(Communicated by Professor W. M. Hicks, F.R.S. Received February 10,—  
Read March 5, 1908.)

(Abstract.)

The main subject of the work described in the present paper consists in the examination of the streamers in the inductive spark in the monochromatic lights of the various metallic lines. It thus forms an extension of the research of Messrs. Schuster and Hemsalech,\* in which the examination of the streamers was restricted to the inductionless spark. The observations were taken by photographing the spectrum as drawn out by a rotating mirror, the slit of the spectroscope being removed and replaced by the spark itself, so that each line of the spectrum formed a monochromatic image of the spark. In order to avoid the superposition of the series of streamers which are formed in the drawing out of each monochromatic image, an arrangement of the prisms of the spectroscope was used by which, while the images of the spark on the camera screen were vertical, and drawn out in a horizontal direction, the dispersion of the spectrum was in a direction of  $45^\circ$  to the horizontal. By this arrangement the series of streamers corresponding to each metallic line becomes distinctly separated from the others.

Photographs of the streamers in the spectra of the sparks from the following metallic poles were taken, in each case with a number of different inductances in series with the spark: aluminium, antimony, bismuth, cadmium, calcium, copper, lead, magnesium, mercury, nickel, platinum,

\* 'Phil. Trans.,' A, vol. 193, p. 189 (1900).

sodium, tin. The chief conclusions which are drawn from the research are as follows :—

(1) The streamers in the inductive spark consist of metallic vapour, the atoms of which are charged, and the motion of the vapour towards the centre of the spark gap is mainly due to the action of the electric force of the spark on the charged atoms. The chief evidence in support of this consists in a number of photographs in which the streamers move back again towards the poles as the oscillating electric field of the spark reverses its direction.

(2) Very great differences were found in the appearances of the streamers which correspond to the different lines of the same metal. The streamers may be divided in this respect into three classes, between which there is in most sparks a sharp distinction :—

(a) Blurred streamers, which are often partly masked by the whole spark gap being filled with their light. These invariably correspond to lines prominent in the arc. (b) Sharply-defined streamers, which appear throughout the whole time during which the electrical discharge lasts. These correspond to pure spark lines, *i.e.*, lines which are not present in the arc under ordinary conditions. (c) A third class of streamers show very brightly at the first oscillation, but fade away so rapidly that they appear for only one or two oscillations, even when the other lines, initially no brighter, show 10 or 12. These lines are very sensitive to the influence of self-induction in the circuit; they are very bright in the condensed spark without inductance, but disappear from the spectrum altogether when a moderate inductance is inserted.

By studying the duration of the lines in the inductionless spark, the difference between the three classes of streamers is found to be solely a question of the duration of the luminosities of the metallic lines to which they correspond, the arc lines having a long, the spark lines a short, and the "condensed spark" lines a very short, duration.

(3) No other difference than this one of the durations of the lines has been discovered in the character of the streamers. The photographs obtained show clearly that the velocities of the streamers corresponding to the different lines in the same spark are the same, in spite of the different character of the streamers.

*Transparent Silver and other Metallic Films.*

By Professor THOMAS TURNER, M.Sc., University of Birmingham.

(Communicated by Professor J. H. Poynting, F.R.S. Received May 9,—Read May 28, 1908.)

## [PLATE 1.]

It is well known that when thin leaves of gold or silver are mounted upon glass and heated to a temperature which is well below a red heat, a remarkable change of properties takes place, whereby the continuity of the metallic film is destroyed. The result is that white light is now freely transmitted, reflection is correspondingly diminished, while the electric resistivity is enormously increased.

A simple method of illustrating this extraordinary change is to mount a sheet of silver leaf between two clean lantern plates, clip them lightly together by means of wire paper fasteners or other suitable means, and then heat gradually to a temperature of not more than 500° C. This can be done conveniently by placing the plates on a thin fire-brick in a cold gas muffle, and then raising the temperature to the desired point. The gas should now be turned off, and the glass plates allowed to cool slowly, so as to avoid cracking. They can then be bound with strips like an ordinary lantern plate, and a permanent example of transparent silver is obtained. It will be found that such a plate transmits the light of the electric lantern almost as readily as ordinary glass, and does not produce any change of colour. The great transparency of the film may be shown by placing the plate upon printing or writing, and photographing the characters through the plate. Every detail of the characters can be reproduced with remarkable clearness. At first sight it is perhaps difficult to conceive that so distinct an impression could be obtained through what was originally a perfectly opaque sheet of silver, and which has only been once heated to a moderate temperature.

The properties of thin metallic films have already been studied by a number of observers and from several points of view. Thus Faraday, in his classical Bakerian Lecture,\* dealt with finely-divided metals in connection with the undulatory theory of light. G. T. Beilby, starting from Faraday's observations, studied the properties of annealed gold leaf,† and afterwards showed the bearing of such facts on the hard and soft states of metals,‡ while

\* 'Phil. Trans.,' 1857, p. 145.

† 'Roy. Soc. Proc.,' 1903, p. 226.

‡ 'Phil. Mag.,' 1904, vol. 8, p. 258.

Garnett has given at length the mathematical considerations arising out of the work of Faraday and Beilby.\* Films of other metals have received attention, as in the work of Wood,† who deals with alkali metal films produced *in vacuo*, and Stone,‡ who describes the formation and properties of thin films of platinum. Another branch of the subject is that of finely-divided metals in solution or suspension; on this there is a voluminous literature. In connection with a closely-allied branch of the subject, it may be recalled that Sir H. Davy, in 1813, showed that the colours produced during the tempering of steel were due to oxidation,§ while the author proved that the colours so obtained depend upon both time and temperature. It was also further suggested that the film of oxide so produced was transparent.||

*Transparent Gold.*—In Faraday's experiments the gold leaf was usually mounted on a single sheet of glass. The alloy was 924 parts gold, 24 parts silver, and 12 parts copper; it was beaten so that 278,000 sheets would be required to make a thickness of 1 inch. In this state it transmitted green light; but it lost its green colour, and transmitted white light when heated in a bath of oil for a few hours to as high a temperature as the oil would bear. The same result was obtained though the supporting material was changed and the surrounding medium replaced by air or by carbon dioxide. It was also found that gold leaf, rendered colourless by heating in a muffle, again transmitted green light after being burnished.

In tests conducted by Mr. Dixon under the direction of the author, the gold leaf employed was 975 fine, and its thickness, as determined by weighing, was such as would require 303,000 sheets to make 1 inch. It was mounted between two microscopic slide glasses, and heated in a glass tube surrounded by an outer iron tube. The temperatures were determined by placing a thermo-electric couple in contact with the upper surface of the glass slide. Under these conditions it was found that gold leaf may be kept at a temperature of 500° C. for half an hour or more without undergoing any appreciable change other than that of annealing, which is an entirely different effect, and which, as observed by Beilby, occurs at about 275°¶ At 550° the green colour begins to fade in a few minutes in air, and still more rapidly in hydrogen.

The nature of the change which occurs in the case of gold is made evident

\* 'Phil. Trans.,' 1904, p. 385.

† 'Phil. Mag.,' 1902, vol. 3, p. 397.

‡ 'Phys. Review,' July, 1905.

§ 'Thomson's Annals,' vol. 1, p. 131.

|| 'Phil. Soc. Birm. Proc.,' vol. 6 (1889), part 2, p. 296.

¶ 'Roy. Soc. Proc.,' A, 1907, vol. 79, p. 467.

by the microphotograph, fig. 1. In annealed gold leaf the structure is, as shown by Beilby, a crystalline network filled in with translucent amorphous metal. But the microphotograph of gold leaf, heated to  $550^{\circ}$ , shows non-crystalline dark parts where the gold has aggregated and white clear parts of plain glass. The gold itself is therefore opaque, instead of being translucent, and the white light passes through the intermediate clear spaces.

In the case of a soft gold cornet from "parting," the change on heating appears to be a gradual one, and not to present any breaks or sudden changes. Even at  $100^{\circ}$  the cornet shrinks and hardens somewhat, and this change increases up to  $750^{\circ}$ , by which point the metal has acquired a brilliant yellow lustre and a distinct granular structure when viewed under the microscope. No change has been observed in a cornet at about  $550^{\circ}$  which corresponds to the marked alteration which occurs in gold leaf at this temperature.

*Transparent Silver.*—Faraday's observations with gold appear to have led him, and subsequent observers, to conclude that the change which takes place when silver is heated would be equally independent of the nature of the surrounding atmosphere. The nature of the gas in which silver is heated has, however, a profound influence on the result, and of this it is now proposed to furnish experimental evidence.

Perhaps the simplest method of procedure is to introduce a sheet of silver foil into a dry test-tube, and to heat the tube till the glass just begins to soften. It will then be found that the silver leaf has shrunk considerably in size; that it has become white and frosted in appearance, thus losing much of its metallic lustre; and that it is now sufficiently transparent to allow of objects being readily seen through its texture. It will also be noted that the change is not confined to any one part of the metal, but that it takes place just as readily away from as near to the glass. But if the experiment be repeated with a tube which is filled with coal gas or with hydrogen, it will be seen that the silver retains its metallic lustre and opacity, and only decreases slightly in bulk. Starting from this simple observation, experiments have been made with the object of determining the temperature at which this remarkable change occurs and the conditions under which it takes place.

The silver leaf used in these experiments was the purest commercially obtainable. It was found by cupellation assay to be 995.1 fine; and when it was dissolved in nitric acid, and precipitated by hydrochloric acid, the solution gave but the faintest discoloration when tested with sulphuretted hydrogen or ammonium sulphide. Subsequent experiments appear to indicate that the only impurity present in appreciable quantity was a trace



of oily matter from the process of beating. Its thickness, as determined by weighing, was such as would require 120,000 sheets to make an inch.

In preliminary tests to determine the temperature at which the change from the opaque to the transparent state took place in air, sheets  $4\frac{1}{4}$  inches square were heated in a muffle. But in subsequent experiments, to ensure greater accuracy, the silver leaf was mounted between two ordinary microscope slides of glass 3 inches by 1 inch. In mounting silver thus between two sheets of glass, special difficulty is met with if the glass surfaces are perfectly smooth and true. The slightest sliding of one glass over the other during mounting is then apt to produce innumerable cracks or fissures in the metal. There is also the disadvantage that the air or other gas employed can only diffuse with extreme slowness. It is easier to work with at least one of the slides of commoner glass, or, otherwise, after placing the silver on the lower side to sprinkle upon it a minute quantity of powdered glass, which has been previously passed through the 100 sieve. An air-space of something under one-hundredth of an inch in thickness is thus ensured, and experience has proved this to be ample.

The samples so mounted were then placed inside a small open cast-iron box, and were supported to allow of the introduction of a thermo-couple under the specimen and above, but near to the bottom of the box. The box was then placed in a cold muffle, and the temperature raised to the desired point, when the sample was removed and allowed to cool at once to the temperature of the air. One important incidental advantage in the use of microscope slide glasses is that the danger of cracking during heating and cooling is very slight, while with the larger glass plates disappointment from fracture during cooling is not unusual.

In these experiments no change was observed in the properties of the silver at temperatures below  $200^{\circ}\text{C}$ , but at  $240^{\circ}$  transparency commenced, and this was practically complete at about  $390^{\circ}$ . The change is a gradual one, and depends upon both time and temperature. A sample heated to  $400^{\circ}$  as rapidly as is safe on a glass slide, or, say, in about 10 minutes, is then quite transparent. To render this gradual change apparent, a series of samples was arranged, and these were laid upon sensitised photographic plates. They were all exposed to the same standard light, and developed in exactly the same manner. A few of the results are given in fig. 2, from which it will be seen that some light began to pass after the sample had been heated to  $240^{\circ}$  transparency increased at  $260^{\circ}$ ; became marked at  $335^{\circ}$ ; and was practically complete at  $390^{\circ}$ . In each case the temperature employed was written in ink on the back of the glass slide, and the clearness with which these figures can be read is a simple measure of the relative transparency.

Silver remains quite opaque, if heated in coal gas to about the same temperature as would render the metal quite transparent if heated in air; and, even at  $500^{\circ}$ , no change is observed in an atmosphere of coal gas. Silver which has been made transparent by heating in air does not become opaque if heated in coal gas to  $510^{\circ}$ , though it is very slightly darkened in colour, and a transparent yellow stain is produced on parts of the glass. Very little effect is produced when silver is heated in charcoal powder for half an hour at  $500^{\circ}$ , while the metal may be heated in hydrogen to  $400^{\circ}$  without sensible alteration.

The structure of transparent silver, when viewed under the microscope, is seen in fig. 3, which shows the appearance of silver leaf heated between glass slides for a few minutes to  $390^{\circ}$ . In this case the change has progressed to such an extent that it is practically complete. The magnification is the same as was employed for the specimens of gold, and on comparison it will be noted that the aggregations in the case of silver are much smaller than with gold, and the opacity of these separate particles is much less marked.

In another series of experiments, silver leaves were heated in a porcelain boat in a combustion tube, in an atmosphere of oxygen which had been previously passed through potash and strong sulphuric acid. It was found that the silver became transparent at about the same temperature, and at least as readily as when heated in air. When still higher temperatures were employed, it was found that leaves of silver, if rolled up into small balls and heated in hydrogen to  $750^{\circ}$ , shrunk in size, and resembled in texture annealed cornets from gold assaying, the opacity and lustre being retained. But when heated in air to  $750^{\circ}$  the leaves crumbled down to a nearly white powder which occupied much less space than in the previous experiment. It would therefore appear that oxygen is necessary for the production of this remarkable change; that the nitrogen of the atmosphere plays no part in the action; and that the nature of the supporting material may be changed without affecting the result.

When transparent silver is examined under the microscope, with moderately high magnification, it is found to have a somewhat arborescent form, and the separate granular masses appear to have some measure of transparency when viewed by transmitted light. This fact, together with what has been above stated, appeared to point to the formation of an oxide of silver which is transparent. Gravimetric experiments were therefore conducted in which carefully weighed quantities of silver leaf were heated in air or oxygen for various times and to gradually increasing temperatures. The conclusions arrived at were entirely negative. The weight taken was usually about 0.125 gramme; sometimes a very slight loss was observed, followed by a

slight gain. But the maximum loss was never more than 1 milligramme, and the maximum gain was also never more than a milligramme. As the leaves were contained in a weighed porcelain boat, the differences observed were not much in excess of the experimental error, and the maximum gain in weight was not more than one-tenth of what would be required for the formation of silver oxide ( $\text{OAg}_2$ ). Evidence that at least much of the silver is still in the metallic state is afforded by the fact that with careful burnishing the lustre and opacity are restored over parts of the glass, while the white powder evolves copious brown fumes when treated with nitric acid.

The method of experimenting was now changed, and four leaves of silver weighing about 0.125 gramme were placed in a glass tube and heated, *in vacuo*, to  $500^\circ$ , and kept at that temperature for 10 minutes. The metal, on cooling, was unchanged in appearance and bulk. There was, in this case, a very slight depression of not more than 3 mm. observed on the gauge of the Sprengel pump, and a slight sublimate was obtained. Under the microscope this was seen to consist of minute oily globules, due apparently to a trace of fatty matter from the goldbeater's skin.

As the metal was unchanged when heated *in vacuo*, oxygen was admitted to a pressure of  $1/5$  of an atmosphere, this corresponding with the amount of oxygen present in air. The metal was heated to  $400^\circ$  and maintained at this temperature for five minutes. On cooling it was found to be completely changed into a white more or less powdery material of much diminished bulk. The change took place in a similar manner when the pressure of oxygen was reduced to  $1/25$  of an atmosphere; and also, though perhaps with less readiness and completeness, when the pressure of oxygen was only 15 mm. In each case the height of the mercury gauge was observed at the beginning of the experiment, and also at the end when the tube had again cooled down, and in no case was any appreciable alteration noticed in the volume of the oxygen.

Whatever the exact nature of the change which takes place may be it is evident that though oxygen is necessary the metal does not increase in weight or the oxygen change in volume.

In seeking for an explanation of an action of oxygen on silver, which does not lead to an increase of weight, reference may be made to some experiments of Plattner mentioned by Dr. Percy,\* in which it was found that finely divided silver when heated to moderate redness in a stream of oxygen yielded a sublimate of metallic silver; it was also shown that oxide of silver is decomposed if heated in oxygen. Dr. Percy carefully repeated Plattner's experiments, but with negative results, so far as a sublimate of silver is

\* 'Gold and Silver,' p. 18.

concerned. Probably in the absence of temperature measurements the conditions were not identical, as there is evidence of the volatility of silver at relatively low temperatures. Thus Professor Richards\* states that silver shows signs of vaporisation when heated *in vacuo* in quartz vessels to 680° C. In the author's experiments on a number of occasions a minute sublimate was obtained when silver was heated in a combustion tube in a current of air or oxygen to somewhat above the point at which transparency is practically complete. This sublimate had every appearance of being white metallic crystals when viewed under the microscope, and a photograph of such a mirror at a magnification of about 120 diameters is given in fig. 4. It appears probable, therefore, that at temperatures ranging from about 240° to 400° C. very finely divided silver combines with oxygen, but that the oxide so produced is again decomposed, the result being the production of metallic silver in a peculiar amorphous condition, in which it is transparent in moderate thicknesses. At the same time, there is sometimes a very minute, though appreciable, volatilisation of the metal, especially when it is heated to about 700° in a current of air.

[*Added July 16.*—It may be added that transparency can only be produced with thin sheets of silver. The thinnest sheets obtained by rolling are about 1/2000 to 1/3000 inch in thickness. Tests made with sheets of silver about 1/2300 and 1/2800 inch in thickness have shown that no transparency is observed even after heating in air or oxygen to 500° for 24 hours. By beating such sheets, leaves of about 1/10000 inch in thickness are obtained; but these, too, show no transparency on heating. Assuming the action to take place equally on each side of the leaf, it follows, therefore, that it does not penetrate to a depth of 1/20000 inch. In other words, it has been proved to occur, in the earlier experiments, through a thickness of about 4/1000000 inch; it has also been shown not to take place through 50/1000000 inch. The intermediate thicknesses have yet to be examined.]

*Transparent Copper.*—The examination of the effect of varying temperatures under different conditions upon other metals, in the form of thin leaf, was a natural result of the preceding observations. The first metal taken for this purpose was copper, which was obtained of a thickness of about 1/75000 inch. The metal was practically pure, as on analysis no trace of other metals could be observed in the necessarily moderate weights employed; tested volumetrically against electrolytic copper it decolorised exactly the correct volume of standard solution of potassium cyanide. This copper leaf when heated between glass slides in coal gas, in hydrogen, or

\* 'Electro-Chem. and Metall.,' 1908, p. 115.

when embedded in fresh charcoal powder, retained its metallic lustre and opacity unimpaired. But when heated in air it gradually assumed the well-known succession of colours, including orange, red, purple, blue, and green. These colours repeated themselves in order several times, each time becoming less separate and distinct. On examining the specimen by transmitted light, as by holding it up by daylight to a window, it was found that in parts a remarkable transparency had been obtained. The first effect is the production of an emerald green colour of great transparency and brilliancy; with further heating this passes into a light olive, then into a darker shade, and ultimately into a dark port wine colour. It is easy to obtain the whole of these transparent colours by heating the sample somewhat rapidly, when the coloured films will form round the outside of the sheet, while in the middle of the plate will be left a small island of untarnished copper. If the sample be now rapidly cooled and examined, it will be found that a brilliant transparent green band surrounds the unaltered metal, while the other shades tone off to a dark reddish transparent brown at the edges.

A simple method of studying the nature of the change is to take a glass beaker about 6 inches high, and suspend vertically in the centre of this a leaf of copper between two glass slides. This will leave about  $1\frac{1}{2}$  inches clear at the top and bottom. The beaker should be covered with a sheet of asbestos board, and surrounded with a thin sheet of asbestos, except for two holes, one on either side, to act as windows. On heating the beaker from below with a bunsen burner a temperature of about  $185^{\circ}$  should be obtained in the centre of the beaker; the top of the slides will then be at about  $160^{\circ}$  and the bottom at about  $215^{\circ}$ . On maintaining the heat for about an hour it will be found that the lower half of the copper is now quite transparent, and transmits a light green or olive colour, while the upper part is almost unaffected and opaque. In the middle of the slide the opaque gradually passes into the transparent form.

The effect produced when copper is heated in air or oxygen depends both upon time and temperature. Below about  $160^{\circ}$  the effect is very slight; above  $400^{\circ}$  it is so rapid as to be scarcely under control. By careful heating between  $200^{\circ}$  and  $250^{\circ}$  any desired shade of surface coloration, or of transparency, may be obtained by suitably adjusting the time of exposure.

The action in the case of copper appears to be quite different from that of silver. Both metals retain their lustre and opacity when heated in hydrogen, in coal gas, or in fresh charcoal powder. But when copper is heated in air there is a gradual increase of weight from the beginning of the action, and ultimately the weight of oxygen absorbed corresponds with that necessary to form the black oxide ( $\text{CuO}$ ). This oxide, though very dark in colour,



FIG. 1.—Transparent gold leaf. 200 V. (Transmitted light.)



FIG. 2 (1).—Silver heated in air to 240° C.



FIG. 2 (2).—Silver heated in air to 260° C.



FIG. 2 (3).—Silver heated in air to 335° C.



FIG. 2 (4).—Silver heated in air to 390° C.



FIG. 2 (5).—Silver made transparent and reheated in coal gas to 510° C.



FIG. 2 (6).—Silver heated in charcoal powder.



FIG. 3.—Transparent silver. 200 V. (Transmitted light.)

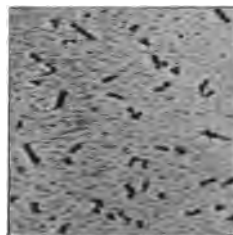


FIG. 4.—Sublimate from heating silver in air. (Mag. 120 diameters.)



transmits a deep olive colour when in sufficiently thin plates. The transparency of the copper is more marked during the early stages of the absorption of oxygen. When copper which has thus been made transparent is heated in coal gas or hydrogen, it becomes once more opaque and recovers its metallic lustre; but the metal is full of minute cracks through which some white light passes and its reflecting power is considerably impaired. That the transparent film obtained on heating copper leaf in air still contains metallic copper can be proved in a very simple manner, namely, by the action of dilute nitric or sulphuric acid (5 to 10 per cent.) upon the transparent coloured material. The acid causes the immediate separation of bright lustrous metallic copper. At the same time the yellow colour disappears from the film while the copper itself transmits white light.

*Aluminium.*—The thinnest sheet of aluminium which is commercially available is about  $1/60000$  inch in thickness, as determined by weighing several leaves. This may be heated between glass slides in air to any temperature up to  $500^{\circ}$  without showing any appreciable diminution of its opacity, and the surface oxidation is apparently slight, even at the higher limit, during one hour.

*Dutch Metal.*—Leaves of Dutch metal, of a thickness of  $1/37000$  inch, were heated to various temperatures, and for different periods in air between glass slides. Very beautiful surface colorations can be thus obtained, but no transparency was observed. With the higher temperatures, however, a certain amount of "skeletonizing," due to the formation of cracks, was usually developed. From this result it is probable that zinc, like aluminium, does not become transparent when heated in oxygen.

*Sulphides.*—As sulphur produces coloured films on metals, it appeared probable that transparent intermediate products would be obtained by the action of sulphuretted hydrogen in sheet metals. Preliminary experiments in this direction have as yet yielded only negative results.

*Cause of Surface Colorations of Metals.*—The discovery of a transparent stage in the oxidation of copper affords strong support of the view that in all cases where a metal oxidises or tarnishes in such a manner as to produce spectrum colours, this is due to the formation of a transparent film. Gold and silver do not really become transparent, but only aggregate in such a manner as to permit of the passage of light between the heaped up particles; hence there is no surface coloured film. Aluminium and zinc remain opaque; hence again there can be no surface colorations as these metals oxidise. Copper, and, presumably, iron, yield transparent bodies during their oxidation, and hence produce films which are capable of giving the colours of the spectrum.



The author has pleasure in acknowledging his indebtedness to Dr. T. J. Baker for information from which this research originated; to Mr. O. F. Hudson for the preparation of the micro-photographs; and to Mr. J. L. Dixon, Bowen Research Scholar in the Metallurgical Department of the University of Birmingham, for the care with which he has repeated and extended many of the earlier observations.

*The  $\omega$ -Functions, a Class of Normal Functions occurring in Statistics.*

By E. CUNNINGHAM, M.A., Fellow of St. John's College, Cambridge, Lecturer in Applied Mathematics, University College, London.

(Communicated by Professor Karl Pearson, F.R.S. Received May 29,—Read June 25, 1908.)

I.—*Introductory.*

The present paper originated in an attempt to discover the significance of certain functions developed by Professor Karl Pearson in a memoir entitled "A Mathematical Theory of Random Migration," and by him called  *$\omega$ -functions*. They belong to the category of normal functions, and are applied in the memoir named to obtain an expansion to represent a distribution symmetrical about a point in a plane. The distribution is not fixed but depends on a parameter  $\sigma$ , the function  $\omega_{2n}$  being a function of  $x = r/\sigma$ ,  $r$  being the distance from the centre of the distribution. The fundamental differential equation is  $\{d^2/dx^2 + (x+x^{-1})d/dx + 2(n+1)\} \omega_{2n}(x) = 0$ .

In the course of the present investigation it soon appeared that the same function led to solutions of the equation of conduction of heat in two dimensions for the case of symmetry round the origin, the time  $t$  taking the place of  $\sigma^2$ . In fact, it was found that if a solution of that equation is sought in the form  $f(t) \phi(r^2/t)$ , that solution is  $t^{-(n+1)} \omega_{2n}(r^2/4t)$ ,  $n$  being arbitrary. The function  $\omega_{2n}$  is equal to  $e^{-r^2/4t}$  multiplied by a polynomial, and is therefore especially adapted to the solution of the problem of the cooling of an infinite sheet, the temperature at a great distance being always zero.

The next step in the paper is to generalise the  *$\omega$ -functions*; and all the solutions of the equation  $\nabla^2 u = \partial u / \partial t$  are found which are of the form  $f(t) \phi(r^2/t) \Theta$ , where  $\Theta$  is a function of the angular co-ordinates of the point

alone. The result is that, as in other problems,  $\Theta$  is a spherical harmonic, or circular function, in the case of three and two dimensions respectively, that  $f(t)$  is of the form  $t^{-n}$ , while  $\phi(r^2/4t)$  satisfies the generalised equation,

$$d^2y/dx^2 + (z + z^{-1}) dy/dx + (2n - m^2 z^{-2}) y = 0,$$

where  $z = rt^{-\frac{1}{2}}$  or  $xd^2y/dx^2 + (x + 1 + m) dy/dx + (n + \frac{1}{2}m) y = 0$ , if  $x = r^2/4t$ . This equation is solved by the Laplace transformation, and the solution,  $(2\pi i)^{-1} e^{-x} \int e^{-uz} (u+1)^{n+\frac{1}{2}m-1} u^{\frac{1}{2}m-n} du$ , taken round a loop contour from infinity round  $u = 0$ , is denoted by  $\omega_{n-1, m}$ . The asymptotic expansion of  $\omega_{n, m}$  is  $\{e^{-x} (-x)^{n-\frac{1}{2}m} / \Gamma(n - \frac{1}{2}m + 1)\}$

$$\left[ 1 - \frac{n^2 - (\frac{1}{2}m)^2}{x} + \frac{\{n^2 - (\frac{1}{2}m)^2\} \{(n-1)^2 - (\frac{1}{2}m)^2\}}{x^2} - \dots \right],$$

which terminates if either  $n - \frac{1}{2}m$  or  $n + \frac{1}{2}m$  is a positive integer.

Thus the solutions of  $\nabla^2 u = \partial u / \partial t$  in the cases of one, two, and three dimensions respectively are

$$t^{-(n+1)} x^{\frac{1}{2}} \omega_{n+\frac{1}{2}, \frac{1}{2}}(x), \quad t^{-(n+1)} x^{\frac{1}{2}m} \omega_{n, m}(x) \frac{\cos m\theta}{\sin m\theta}, \quad t^{-(n+1)} x^{\frac{1}{2}k} \omega_{n-\frac{1}{2}, k+\frac{1}{2}}(x) \gamma_k(\theta, \phi),$$

$\gamma_k$  being a spherical harmonic of order  $k$ , which reduce for certain values of the constants to simple well-known solutions, viz. :—

- (i) To  $(-\pi t)^{-\frac{1}{2}} e^{-x}$  (for  $n = -\frac{1}{2}$ ),      (ii) to  $t^{-1} e^{-x}$  (for  $n = m = 0$ ),  
(iii) to  $t^{-\frac{1}{2}} e^{-x}$  (for  $n = \frac{1}{2}, k = 0$ ).

The one-dimensional solution obtained is not new, it practically coincides with the function of the parabolic cylinder, or the functions considered by Sturm\* in connection with the conduction of heat, by Thiele and Charlier in reference to probability, and by Hermite.† The two-dimensional functions seem to be new, but they are shown to be the equivalent in polar co-ordinates of the functions considered by Hermite

$$(\partial' / \partial' x)^m (\partial / \partial y)^n e^{-\frac{1}{2}(x^2 + y^2)},$$

and the relations connecting the two types of function are obtained.

It is shown in the paper that any function of  $x$  and  $\theta$  can be expanded in the form

$$\sum \sum a_{n, m} \omega_{n, m} \cos m\theta, \quad \text{where } (-)^m \pi a_{n, m} = \int_0^{2\pi} \int_0^\infty f e^x x^{-\frac{1}{2}m} \omega_{n, -m} \cos m\theta \, dx \, d\theta,$$

and a proof of the convergence and validity of the expansion is given in the case where  $f$  is independent of  $\theta$ , with an indication of the extension to the general case. Hence a series is obtained giving a solution of the equation

\* Liouville, I and II.

† 'Comptes Rendus,' vol. 58.

$\nabla^2 u = \partial u / \partial t$ , which reduces for  $t = t_0$  to a function given all over the plane, viz. :—

$\sum \sum a_{n,m} (t_0/t)^{n+1} \omega_{n,m}(r^2/4t_0) \cos m\theta$ , the coefficient  $a_{n,m}$  being obtained as above. This series is shown, by direct expansion, to be equivalent to Laplace's definite integral solution of the cooling of an infinite plate, viz.,

$$\iint f(\xi, \eta) e^{-[(x-\xi)^2 + (y-\eta)^2]/4(t-t_0)} d\xi d\eta / 4\pi (t-t_0).$$

Various other expansions are given analogous to Neumann's expansions of  $J_n(r^2 + \rho^2 - 2r\rho \cos \theta)^{\frac{1}{2}}$  in a series of Bessel functions.

The last part of the paper considers the equivalent functions in Cartesian co-ordinates, in terms of which Hermite has expanded any function. It is shown that an equivalent method of obtaining Hermite's expansion is that of equating the successive moments of the series to those of the given function, with special reference to obtaining the best fitting surface for a given frequency distribution in two dimensions. The series of approximations so obtained is compared with that of Edgeworth,\* which is ultimately the same, and is shown to converge rapidly under the same conditions. An example is then given of the contour lines of a surface obtained by taking terms up to the fourth order. These contour lines show much similarity with those actually observed in statistical work, such as those given by Perozzo in his memoir.† The possibility of obtaining a fairly close approximation to a given distribution by means of a knowledge of the product moments up to the fourth order is thus established.

## II.—*The Derivation of the Generalised $\omega$ -function.*

1. *The Fundamental Differential Equation.*—In order to obtain the types of function suitable to the problems mentioned, the most general solution of the equation  $\nabla^2 u = \partial u / \partial t$  will be found in the form  $T.R.\Theta$ , where  $T$  is a function of  $t$  alone,  $R$  a function of  $r^2/t$ , and  $\Theta$  of the angular co-ordinates. To begin with, the cases of one, two, and three dimensions are considered separately.

(a) *One Dimension.*—Putting  $z = r^2/t$  in the equation, it becomes

$$4z \frac{\partial^2 u}{\partial z^2} + (z+2) \frac{\partial u}{\partial z} = t \frac{\partial u}{\partial t}.$$

If  $u = Z.T$ ,  $Z$  and  $T$  being functions of  $z$  and  $t$  respectively, we have

$$\left\{ 4z \frac{\partial^2 Z}{\partial z^2} + (z+2) \frac{\partial Z}{\partial z} \right\} Z^{-1} = \frac{t}{T} \frac{\partial T}{\partial t}, \quad (1)$$

so that both sides must be independent of  $t$  and  $z$ .

\* 'Camb. Phil. Trans.,' August, 1904.

† 'Annali di Statistica,' 3A, 5, 1883.

$$\text{Hence } t \frac{\partial T}{\partial t} + nT = 0 \quad \text{and} \quad 4z \frac{\partial^2 Z}{\partial z^2} + (z+2) \frac{\partial Z}{\partial z} + nZ = 0,$$

where  $n$  is any constant. Thus  $T = t^{-n}$ .

(b) *Two Dimensions.*—The equation in polar co-ordinates is

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \frac{1}{r^2} \frac{\partial^2 u}{\partial \theta^2} = \frac{\partial u}{\partial t}.$$

If  $u = \Theta v$  satisfies this equation,  $\Theta$  being a function of  $\theta$  only, and  $v$  being independent of  $\theta$ , the functions  $\Theta$  and  $v$  satisfy

$$\frac{r^2}{v} \left( \frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} + \frac{1}{r^2} \frac{\partial^2 v}{\partial \theta^2} \right) = -\frac{1}{\Theta} \frac{\partial^2 \Theta}{\partial \theta^2} = m^2,$$

$m$  being a constant. Thus  $\Theta = A \sin m\theta + B \cos m\theta$ , and again, putting  $z = r^2/t$ , and  $v = T \cdot Z$ , the same procedure as above gives  $T = t^{-n}$  and

$$4z \frac{\partial^2 Z}{\partial z^2} + (z+4) \frac{\partial Z}{\partial z} + \left( n - \frac{m^2}{z} \right) Z = 0. \quad (2)$$

(c) *Three Dimensions.*—Exactly similar procedure in this case leads to the conclusion that, if  $u = T \cdot Z \cdot \Theta$ ,  $\Theta$  being a function of  $\theta$  and  $\phi$ ,  $\Theta$  must be a spherical harmonic—say of order  $k$ ,  $T$  must be  $t^{-n}$ , and that then  $Z$  satisfies the equation

$$4z \frac{\partial^2 Z}{\partial z^2} + (z+6) \frac{\partial Z}{\partial z} + \left\{ n - \frac{k(k+1)}{z} \right\} Z = 0. \quad (3)$$

(d) *Three Dimensions—Cylindrical Co-ordinates* ( $\rho, \theta, \zeta$ ).—In this system of co-ordinates the general solution is  $\frac{\sin m\theta}{\cos k\zeta} \frac{\sinh k\zeta}{\cosh k\zeta} Z$ , where  $Z$  satisfies the equation

$$4z \frac{\partial^2 Z}{\partial z^2} + (z+4) \frac{\partial Z}{\partial z} + \left( k^2 + n - \frac{m^2}{z} \right) Z = 0. \quad (4)$$

The equations (1) to (4) can be brought under the same form. Putting  $Z = z^{\frac{1}{2}} X$ ,  $z^{\frac{1}{2}+m} X$ ,  $z^{\frac{1}{2}} X$ ,  $z^{\frac{1}{2}+m} X$  in the four cases respectively, and also  $z = 4x$ , the equations become, using dashes to denote differential coefficients,

$$xX'' + (x + \frac{1}{2}) X' + (n + \frac{1}{2}) X = 0, \quad (5)$$

$$xX'' + (x + 1 + m) X' + (n + \frac{1}{2}m) X = 0, \quad (6)$$

$$xX'' + (x + \frac{3}{2} + k) X' + (n + \frac{1}{2}k) X = 0, \quad (7)$$

$$xX'' + (x + 1 + m) X' + (n + k^2 + \frac{1}{2}m) X = 0. \quad (8)$$

Taking (6) as the standard form, the particular solution dealt with in this paper will be denoted by  $\omega_{n-1, m}$ : the corresponding solutions of (5), (7), and (8) are therefore

$$\omega_{n-\frac{1}{2}, \frac{1}{2}}, \quad \omega_{n-\frac{1}{2}, \frac{1}{2}k}, \quad \omega_{k^2+n-1, m},$$

and the complete solutions of the original equations are

$$(9) \ t^{-(n+1)} x^{\frac{1}{2}} \omega_{n+\frac{1}{2}, \frac{1}{2}}(x), \quad (10) \ t^{-(n+1)} x^{\frac{1}{2}m} \frac{\sin m\theta}{\cos} \omega_{n,m}(x),$$

$$(11) \ t^{-(n+1)} x^{\frac{1}{2}k} \omega_{n-\frac{1}{2}, k+\frac{1}{2}}(x) y_k(\theta), \quad (12) \ t^{-(n+1)} x^{\frac{1}{2}m} \omega_{n+k, m}(x) \frac{\cosh kz}{\sinh} \frac{\cos m\theta}{\sin}.$$

The simplest solutions are given in the four cases as follows:—

(i)  $n = -\frac{1}{2}$ , (ii)  $n = 0, m = 0$ , (iii)  $n = \frac{1}{2}, k = 0$ , (iv)  $n = m = k = 0$ .

2. *The Solution of the Fundamental Equation.*—Putting  $X = \int_c e^{-vz} \nabla dv$  and forming the Laplace transformation of the equation, we find that  $V$  must satisfy the equation

$$v(v-1) \partial V / \partial v = \{(m-1)v - (n + \frac{1}{2}m - 1)\} V,$$

giving

$$V = A v^{n+\frac{1}{2}m-1} (v-1)^{\frac{1}{2}m-n},$$

while the contour  $c$  must be such that  $V e^{-vz}(v-v^2)$  has the same value at the two extremities. Assuming  $x$  to be real and positive, this will be attained by taking a contour consisting of a line following the real axis from  $v = \infty$  to  $v = a$  ( $a < 1$ ), then a circle about  $v = 1$  of radius  $a$ , and a straight line returning along the real axis to infinity. A similar contour encircling the point 0 instead of 1 will be denoted by  $\gamma$ . Putting  $u = v-1$  and  $A = \frac{1}{2}\pi i$ , we have for  $\omega_{n,m}$  the expression  $(\frac{1}{2}\pi i) e^{-x} \int_{\gamma} e^{-uz} (u+1)^{n+\frac{1}{2}m} u^{\frac{1}{2}m-n-1} du$ .

The integral gives the asymptotic expansion for  $\omega_{n,m}$

$$(13) \quad \frac{e^{-x} (-x)^{n-\frac{1}{2}m}}{\Gamma(n-\frac{1}{2}m+1)} \left\{ 1 - \frac{(n+\frac{1}{2}m)(n-\frac{1}{2}m)}{x} + \frac{(n+\frac{1}{2}m)(n+\frac{1}{2}m-1)(n-\frac{1}{2}m)(n-\frac{1}{2}m-1)}{2! \cdot x^2} - \dots \right\},$$

which terminates if either  $n - \frac{1}{2}m$  or  $n + \frac{1}{2}m$  is a positive integer

The most important case is that in which  $n - \frac{1}{2}m$  is a positive integer; in that case

$$(14) \quad \omega_{n,m} = e^{-x} \Gamma(n+\frac{1}{2}m+1) \left\{ \frac{1}{\Gamma(m+1)(n-\frac{1}{2}m)!} - \frac{x}{\Gamma(m+2)1!(n-\frac{1}{2}m-1)!} + \dots (-)^{n-\frac{1}{2}m} \frac{x^{n-\frac{1}{2}m}}{\Gamma(n+\frac{1}{2}m+1)(n-\frac{1}{2}m)!} \right\}.$$

In particular, if  $m = 0$  this reduces to Pearson's function  $\omega_{2n}$ .

When  $n - \frac{1}{2}m$  is half an odd integer,  $\omega_{n,m}$  becomes purely imaginary. This case occurs below, but no difficulty arises on that account.

Especially important is the case in which both  $n - \frac{1}{2}m$  and  $n + \frac{1}{2}m$  are integers, for then we have the relation,

$$(15) \quad (-x)^{\frac{1}{2}m} \omega_{n,m} / \Gamma(n+\frac{1}{2}m+1) = (-x)^{-\frac{1}{2}m} \omega_{n,-m} / \Gamma(n-\frac{1}{2}m+1).$$

3. *Relations connecting Successive Functions.*—(a) *Difference equations*—

$$\begin{aligned}
 2\pi i x d\omega_{n-1, m}/dx &= - \int_{\gamma} (u+1)^{n-\frac{1}{2}m} u^{-n-\frac{1}{2}m} e^{-(1-u)x} x du \\
 &= - \int_{\gamma} \partial/\partial u \{ (u+1)^{n-\frac{1}{2}m} u^{-n-\frac{1}{2}m} \} e^{-(1+u)x} du \\
 &= 2\pi i \{ (n+\frac{1}{2}m) \omega_{n, m} - (n-\frac{1}{2}m) \omega_{n-1, m} \}.
 \end{aligned}$$

Thus  $x d\omega_{n-1, m}/dx + (n-\frac{1}{2}m) \omega_{n-1, m} = (n+\frac{1}{2}m) \omega_{n, m}$ . (16)

Applying this twice and simplifying by means of the fundamental differential equation, we find

$$(n+\frac{1}{2}m) \omega_{n, m} - (2n-x-1) \omega_{n-1, m} + (n-\frac{1}{2}m-1) \omega_{n-2, m} = 0. \quad (17)$$

(b) *The Expression of  $\omega_{n, m}$  as a Differential Coefficient.*—Since the derivative of any solution of  $\nabla^2(u) = \partial u/\partial t$  with respect to  $t$  is also a solution, and since  $\partial/\partial t \{ t^n f(r^2/t) \} = t^{n-1} \phi(r^2/t)$ , we deduce at once, after adjusting the numerical coefficients, the following relations in the cases of one, two, and three dimensions respectively (*vide* (9), (10), (11))—

$$\partial/\partial t \{ t^{-n} x^{\frac{1}{2}} \omega_{n-\frac{1}{2}, \frac{1}{2}}(x) \} = -n t^{-n-1} x^{\frac{1}{2}} \omega_{n+\frac{1}{2}, \frac{1}{2}}(x), \quad (18)$$

$$\partial/\partial t \{ t^{-n} x^{\frac{1}{2}} \omega_{n-1, m}(x) \} = -(n-\frac{1}{2}m) t^{-n-1} x^{\frac{1}{2}} \omega_{n, m}(x), \quad (19)$$

$$\partial/\partial t \{ t^{-n} x^{\frac{1}{2}} \omega_{n-\frac{1}{2}, k+\frac{1}{2}}(x) \} = -(n-\frac{1}{2}k) t^{-n-1} x^{\frac{1}{2}} \omega_{n-\frac{1}{2}, k+\frac{1}{2}}(x). \quad (20)$$

III.—*The Linear Function  $\omega_{n+\frac{1}{2}, \frac{1}{2}}$* 

1. Restricting the work in this section to the functions arising in the one-dimensional case, which are briefly called the *linear  $\omega$ -functions*, it will be convenient to write  $\omega_r$  for  $\omega_{n-\frac{1}{2}, \frac{1}{2}}$  and  $\omega'_r$  for  $\omega_{n-\frac{1}{2}, -\frac{1}{2}}$ , and  $\nu$  in place of  $n$ .

From (18) we then have

$$\begin{aligned}
 t^{-\nu-\frac{1}{2}} x^{\frac{1}{2}} \omega_r &= (-\partial/\partial t)^{\nu} \{ t^{-\frac{1}{2}} x^{\frac{1}{2}} \omega_0(x) \} \Gamma(\frac{1}{2})/\Gamma(\nu+\frac{1}{2}) \\
 &= (-)^{\nu-\frac{1}{2}} (\partial/\partial t)^{\nu} (t^{-\frac{1}{2}} e^{-x})/\Gamma(\nu+\frac{1}{2}) = (-)^{\nu-\frac{1}{2}} (\partial/\partial r)^{2\nu} (t^{-\frac{1}{2}} e^{-r^2/4t}),
 \end{aligned}$$

assuming that  $\nu$  is an integer. If  $\nu-\frac{1}{2}$  is an integer, we have, similarly,

$$\begin{aligned}
 t^{-\nu-\frac{1}{2}} x^{\frac{1}{2}} \omega_r &= (-)^{\nu-\frac{1}{2}} (\partial/\partial t)^{\nu-\frac{1}{2}} \{ t^{-\frac{1}{2}} x^{-\frac{1}{2}} \omega_{\frac{1}{2}}(x) \} / \Gamma(\nu+\frac{1}{2}) \\
 &= (-)^{\nu-\frac{1}{2}} (\partial/\partial r)^{2\nu-1} \{ \frac{1}{2} t^{-\frac{1}{2}} r e^{-r^2/4t} \} = (-)^{\nu-\frac{1}{2}} (\partial/\partial r)^{2\nu} (t^{-\frac{1}{2}} e^{-r^2/4t}).
 \end{aligned}$$

Thus in either case

$$\omega_{\frac{1}{2}r} = (-)^{\nu-\frac{1}{2}} (\partial/\partial r)^{\nu} (e^{-r^2/4t})/r \Gamma\{\frac{1}{2}(\nu+1)\}. \quad (21)$$

Thus, as a function of  $r$ ,  $\omega_{\frac{1}{2}r}$  is identified with the function considered by Hermite.\*

\* 'Comptes Rendus,' vol. 68.

2. *An Expansion in a Series of Linear  $\omega$ -Functions.*—The expansion of  $\omega_{\frac{1}{2}\nu}$  is  $\frac{e^{-x}(-x)^{\frac{1}{2}(\nu-1)}}{\Gamma\{\frac{1}{2}(\nu+1)\}} \left\{ 1 - \frac{\nu(\nu-1)}{4x} + \frac{\nu(\nu-1)(\nu-2)(\nu-3)}{2!(4x)^2} \dots \right\}$ , which, if  $\nu$  is an odd integer, becomes

$$e^{-x} \frac{\nu!}{2^{\nu-1}\Gamma\{\frac{1}{2}(\nu+1)\}} \left\{ \frac{1}{\frac{1}{2}(\nu-1)!} - \frac{4x}{\frac{1}{2}(\nu-3)!3!} + \dots - \frac{(-4x)^{\frac{1}{2}(\nu-1)}}{\nu!} \right\},$$

and if  $\nu$  is an even integer,

$$e^{-x} \frac{\nu!(-x)^{-\frac{1}{2}}}{2^{\nu}\Gamma\{\frac{1}{2}(\nu+1)\}} \left\{ \frac{1}{\frac{1}{2}\nu!} - \frac{4x}{\frac{1}{2}(\nu-2)!2!} + \dots - \frac{(4x)^{\frac{1}{2}\nu}}{\nu!} \right\}.$$

Hence,  $\omega_{\frac{1}{2}\nu}$  = coefficient of  $q^{\nu}$  in  $\nu! e^{q^2+2iq\sqrt{x}-x}/(-x)^{\frac{1}{2}} 2^{\nu}\Gamma\{\frac{1}{2}(\nu+1)\}$ ,  
and therefore

$$x^{-\frac{1}{2}} e^{q^2-x} \cos 2q\sqrt{x} = i \sum (2q)^{\nu} \Gamma\{\frac{1}{2}(\nu+1)\} \omega_{\frac{1}{2}\nu} / \Gamma(\nu+1) = i \sum q^{\nu} \omega_{\frac{1}{2}\nu} \Gamma(\frac{1}{2}) / \Gamma(\frac{1}{2}\nu+1) \quad (22)$$

and

$$x^{-\frac{1}{2}} e^{q^2-x} \sin 2q\sqrt{x} = \sum (2q)^{\nu} \Gamma\{\frac{1}{2}(\nu+1)\} \omega_{\frac{1}{2}\nu} / \Gamma(\nu+1) = \sum q^{\nu} \omega_{\frac{1}{2}\nu} \Gamma(\frac{1}{2}) / \Gamma(\frac{1}{2}\nu+1), \quad (23)$$

the former summation being for even values of  $\nu$  and the latter for odd, or together,

$$x^{-\frac{1}{2}} e^{(q+\sqrt{x})^2} = \sqrt{-\pi} \sum_{\nu=0}^{\infty} (q)^{\nu} \omega_{\frac{1}{2}\nu} / \Gamma(\frac{1}{2}\nu+1). \quad (24)$$

3. *Application of the above Expansion.*—The foregoing properties will now be applied to obtain an expansion of Laplace's solution of the problem of the cooling of an infinite bar. We have

$$\begin{aligned} \{2\pi(t-t_0)\}^{-\frac{1}{2}} e^{-(r-\rho)^2/4(t-t_0)} &= (2\pi)^{-1} \int_{-\infty}^{\infty} e^{-u^2(t-t_0)-iur(r-\rho)} du \\ &= (4\pi)^{-\frac{1}{2}} i \int_{-\infty}^{\infty} e^{-u^2 t - iur \rho} \rho e^{\rho^2/4t_0} \sum u^{\nu} t_0^{(\nu-1)/2} \omega_{\frac{1}{2}\nu}(\rho^2/4t_0) du / \Gamma(\frac{1}{2}\nu+1), \\ &= (4\pi)^{-\frac{1}{2}} \rho e^{\rho^2/4t_0} \sum (-t_0)^{\frac{1}{2}(\nu-1)} \omega_{\frac{1}{2}\nu} / \Gamma(\frac{1}{2}\nu+1) (\partial/\partial r)^{\nu} \int_{-\infty}^{\infty} e^{-u^2 t - iur} du, \\ &= (2t_0)^{-\frac{1}{2}} e^{\rho^2/4t_0} (\rho^2/4t_0)^{\frac{1}{2}} (r^2/4t)^{\frac{1}{2}} \sum (t_0/t)^{(\nu+1)/2} \omega_{\frac{1}{2}\nu}(\rho^2/4t_0) \omega_{\nu}(r^2/4t) \\ &\quad \Gamma\{\frac{1}{2}(\nu+1)\} / \Gamma(\frac{1}{2}\nu+1), \\ &= (-2t_0)^{-\frac{1}{2}} e^{\xi} \xi^{\frac{1}{2}} \sum (t_0/t)^{\nu+1} \omega'_{\frac{1}{2}\nu}(\xi) \omega_{\frac{1}{2}\nu}(x), \end{aligned}$$

using (15) and putting  $\xi$  for  $\rho^2/4t_0$ .

Now, as Laplace as shown,  $V = \int_{-\infty}^{\infty} f(\xi) (4\pi t)^{-\frac{1}{2}} e^{-(x-\xi)^2/4t} d\xi$  is a function of  $x$  satisfying  $\partial^2 V / \partial x^2 = \partial V / \partial t$  and reducing when  $t = 0$  to  $f(x)$ . Putting  $(t-t_0)$  in place of  $t$ , and expanding the subject of integration as above, we obtain

the following series to represent a solution of the same equation reducing when  $t = t_0$ , to  $f(x)$ :

$$\sum a_v (t_0/t)^{\frac{1}{2}(v+1)} x^{\frac{1}{2}} \omega_v(x), \quad (25)$$

where

$$a_v = -\frac{1}{2}i \int_{-\infty}^{\infty} f(\rho) e^{\frac{1}{2}\xi^2} \omega'_v(\xi) d\xi.$$

In accordance with a remark made above, it may be noted that, when  $\omega_v$  is real,  $\omega'_v$  is imaginary, so that the expansion is wholly real. A different method of establishing the same expansion is given below.

#### IV.—The General $\omega$ -Function—Integral Properties.

Let

$$\begin{aligned} -4\pi^2 I_{n, n', m} &= -4\pi^2 \int_0^{\infty} e^x \omega_{n, m}(x) \omega_{n', -m}(x) dx \\ &= \int_0^{\infty} dx \int_{\gamma} du \int_{\gamma} dv e^{-(u+v+1)x} (u+1)^{n+\frac{1}{2}m} u^{\frac{1}{2}m-n-1} (v+1)^{n'-\frac{1}{2}m} v^{-\frac{1}{2}m-n'-1}. \end{aligned}$$

The asymptotic expansion of the  $\omega$ -function shows that the integration in regard to  $x$  to the infinite upper limit is valid, and the order of integration may be inverted. Thus

$$-4\pi^2 I_{n, n', m} = \int_{\gamma} du \int_{\gamma} dv (u+1)^{n+\frac{1}{2}m} u^{\frac{1}{2}m-n-1} (v+1)^{n'-\frac{1}{2}m} v^{-\frac{1}{2}m-n'-1} (u+v+1)^{-1}.$$

For every value of  $v$  the subject of integration is zero to the second order at least when  $u$  is infinite if  $m$  is positive, and *vice versa* if  $m$  is negative. Taking  $m$  positive for the sake of argument,

$$\begin{aligned} -4\pi^2 I_{n, n', m} &= - \int_{-\nu-1}^{\infty} du \int_{\gamma} dv (u+1)^{n+\frac{1}{2}m} u^{\frac{1}{2}m-n-1} (v+1)^{n'-\frac{1}{2}m} v^{-\frac{1}{2}m-n'-1} (u+v+1)^{-1} \\ &= (-)^m 2\pi i \int_{\gamma} dv v^{n-n'-1} (1+v)^{n'-n-1} = (-)^m (-4\pi^2), \end{aligned}$$

if  $n = n'$ , or  $= 0$  if  $n \neq n'$ . Thus

$$\int_0^{\infty} e^x \omega_{n, m}(x) \omega_{n', -m}(x) dx = 0, \quad (26)$$

$$\text{but} \quad \int_0^{\infty} e^x \omega_{n, m}(x) \omega_{n, -m}(x) dx = (-1)^m. \quad (27)$$

Again, consider the moment integral

$$\begin{aligned} 2\pi i M_r &= 2\pi i \int_0^{\infty} \omega_{n, m}(x) x^r dx = \int_0^{\infty} x^r dx \int_{\gamma} e^{-(u+1)x} (u+1)^{n+\frac{1}{2}m} u^{\frac{1}{2}m-n-1} du \\ &= \Gamma(r+1) \int_{\gamma} (u+1)^{n+\frac{1}{2}m-r-1} u^{\frac{1}{2}m-n-1} du. \end{aligned}$$



Thus, if  $n + \frac{1}{2}m - r$  is a positive integer,  $(1+u)^{n+\frac{1}{2}m-r-1}$  is a polynomial and the subject of integration has no residue at  $u = 0$ . But if  $n + \frac{1}{2}m - r$  is zero or a negative integer, the residue is  $(-)^{n-\frac{1}{2}m}(r+1-n-\frac{1}{2}m)\dots(r-m)/(n-\frac{1}{2}m)!$ . Thus

$$M_r = 0, \quad (-1)^{n-\frac{1}{2}m}, \quad (-)^{n-\frac{1}{2}m} (-)^{n-\frac{1}{2}m} \Gamma(r+1) \Gamma(r-m+1)/(n-\frac{1}{2}m)! \\ \Gamma(r-n-\frac{1}{2}m+1), \quad (28)$$

according as  $r <, =, \text{ or } > n + \frac{1}{2}m$ . In this  $r$  is not necessarily an integer, but  $n - \frac{1}{2}m$  and  $n + \frac{1}{2}m - r$  are assumed to be integers.

If these results, (26) and (27), be applied in the one-dimensional case considered above, assuming that  $f(\xi) = \Sigma a_r \xi^r \omega_r(\xi)$ , we obtain at once

$$a_r = -\frac{1}{2}i \int_0^\infty f(\xi) e^{\xi^2} \omega_r'(\xi) d\xi. \quad \text{Consequently, if } \xi = r^2/4t \text{ and } x = r^2/4t, \\ \Sigma a_r (t_0/t)^{n+\frac{1}{2}m} \omega_r(x) \text{ is a function satisfying } \partial^2 u / \partial r^2 = \partial u / \partial t, \text{ and reducing} \\ \text{when } t = t_0 \text{ to the given function } f(x). \text{ Thus the expansion (25) is obtained.}$$

#### V.—*The $\omega$ -Functions in a Plane.*

Coming to the special values of  $n$  and  $m$  suitable to the development of functions in a plane,  $m$  is an integer and  $n - \frac{1}{2}m$  is an integer. Using relation (19), we have

$$\Omega_{n,m} = t^{-(n+1)} (r^2/t)^{-\frac{1}{2}m} \omega_{n,m}(r^2/4t) e^{im\theta} \\ = (-\partial/\partial t)^n \{t^{-1} (r^2/t)^{-\frac{1}{2}m} \omega_{0,m} e^{im\theta}\} \Gamma(\frac{1}{2}m+1)/\Gamma(\frac{1}{2}m+n+1) \\ = \{-\nabla^2\}^n \{t^{-1} (r^2/t)^{-\frac{1}{2}m} \omega_{0,m} e^{im\theta}\} \Gamma(\frac{1}{2}m+1)/\Gamma(\frac{1}{2}m+n+1). \quad (29)$$

In particular, if we start from the function independent of  $\theta$ , i.e. put  $m = 0$ ,  $\Omega_{n,0} = t^{-n+1} \omega_n(r^2/4t) = (-\partial/\partial t)^n (t^{-1} e^{-r^2/4t})/n!$ , so that

$$\omega_n = (-t)^n/n! (\partial^2/\partial r^2 + 1/r \partial/\partial r)^n e^{-r^2/4t}. \quad (30)$$

This particular set of functions may conveniently be called the *zonal  $\omega$ -functions*.

If  $m$  be not zero, but  $n - \frac{1}{2}m$  a positive integer, so that  $\omega_{n,m}$  is polynomial,

$$\Omega_{n,m} = (-\partial/\partial t)^{n-\frac{1}{2}m} \{t^{-(\frac{1}{2}m+1)} (r^2/t)^{-\frac{1}{2}m} \omega_{\frac{1}{2}m,m} e^{im\theta}\} \\ = (-\partial/\partial t)^{n-\frac{1}{2}m} \{r^m t^{-m-1-r^2/4t} e^{im\theta}\} \Gamma(m+1)/\Gamma(\frac{1}{2}m+n+1) \\ = (-)^{n-\frac{1}{2}m} (\nabla^2)^{n-\frac{1}{2}m} \{r^m t^{-m-1} e^{-r^2/4t} e^{im\theta}\} \Gamma(m+1)/\Gamma(\frac{1}{2}m+n+1). \quad (31)$$

Thus all the functions found are expressed in terms of the derivatives of the fundamental function with respect to  $r$ ,  $\theta$ , and  $t$ .

Since the derivatives of any solution of  $\nabla^2 u = \partial u / \partial t$  with respect to Cartesian co-ordinates  $x$  and  $y$  are also solutions, we may expect all solutions to be expressible in terms of the derivatives with respect to  $x$  and  $y$  of the fundamental solution.

The following equations may be shown to hold for the planar  $\omega$ -functions,

$$\Omega_{\frac{1}{2}m, m} = (\partial/\partial x + i\partial/\partial y)^m (t^{-1}e^{-r^2/4t}),$$

and, therefore,  $n - \frac{1}{2}m$  being an integer,

$$\begin{aligned}\Omega_{n, m} &= (\partial^2/\partial x^2 + \partial^2/\partial y^2)^{n-\frac{1}{2}m} (\partial/\partial x + i\partial/\partial y)^m (t^{-1}e^{-r^2/4t}) \\ &= (\partial/\partial t)^{n-\frac{1}{2}m} (\partial/\partial x + i\partial/\partial y)^m (t^{-1}e^{-r^2/4t}),\end{aligned}$$

$$\text{or} \quad (\partial/\partial x + i\partial/\partial y)^{n+\frac{1}{2}m} (\partial/\partial x - i\partial/\partial y)^{n-\frac{1}{2}m} (t^{-1}e^{-r^2/4t}); \quad (32)$$

e.g., we have

$$(\partial^2/\partial x^2 - \partial^2/\partial y^2) (t^{-1}e^{-r^2/4t}) = (4t)^{-1} (r^2/t) e^{-r^2/4t} \cos 2\theta.$$

$$2 \partial^2/\partial x \partial y (t^{-1}e^{-r^2/4t}) = (4t)^{-1} (r^2/t) e^{-r^2/4t} \sin 2\theta,$$

$$\text{and} \quad (\partial^2/\partial x^2 + \partial^2/\partial y^2) (t^{-1}e^{-r^2/4t}) = -(t)^{-1} (1 - r^2/4t) e^{-r^2/4t},$$

giving the values of  $\partial^2/\partial x^2$ ,  $\partial^2/\partial y^2$ ,  $\partial^2/\partial z^2$  in terms of  $\Omega_{10}$  and  $\Omega_{12}$ . Thus the connection is established between the planar  $\omega$ -functions and Hermite's functions  $\partial^{r+s}/\partial x^r \partial y^s \{e^{-a(x^2+y^2)}\}$ , to which reference is made below.

#### VI.—*The Expansion of any Function in Planar $\omega$ -Functions.*

1. Suppose that a function of  $r$  and  $\theta$  may be expanded in the form

$$f(r, \theta) \sum_n \sum_m a_{nm} (x)^{\frac{1}{2}m} \omega_{nm} (x) \cos m\theta + \sum_n \sum_m b_{nm} x^{\frac{1}{2}m} \omega_{n, m} (x) \sin m\theta,$$

where  $x = r^2/4t$ ,  $t$  being a parameter. Then, using the Fourier method for all values of  $m$ , we have

$$\int_0^{2\pi} f(r, \theta) \cos m\theta d\theta = \pi \sum_n a_{nm} x^{\frac{1}{2}m} \omega_{n, m}$$

and

$$\int_0^{2\pi} f(r, \theta) \sin m\theta d\theta = \pi \sum_n b_{nm} x^{\frac{1}{2}m} \omega_{n, m}.$$

In order to find the coefficients  $a_{n, m}$ ,  $b_{n, m}$ , we now use the integrals developed above, and obtain

$$(-)^m \pi a_{n, m} = \int_0^{2\pi} \int_0^\infty f \cdot e^x x^{-\frac{1}{2}m} \omega_{n, -m} \cos m\theta dx d\theta, \quad (33)$$

with a similar expression for  $b_{n, m}$ . Thus, in order to obtain the coefficient of  $\omega_{n, m}$ , we make use of the allied function  $\omega_{n, -m}$ , which bears to it the relation (15).

The values of  $m$  and  $n$  required to be taken do not appear, but it will be shown presently that  $m$  takes all integer values and  $n$  takes those values for which  $n - \frac{1}{2}m$  is zero or a positive integer. The expansion is therefore one in a series of polynomials. The corresponding expansion in Cartesian co-ordinates is given by Hermite.\*

\* 'Comptes Rendus,' vol. 68.

2. *The Expansion of the Laplace Definite Integral in a Plane.*—An expansion analogous to (26) will first be obtained.  $x$  standing, as everywhere, for  $r^2/4t$ , let  $z$  stand for  $re^{i\theta}/2\sqrt{t}$  and  $z'$  for  $re^{-i\theta}/2\sqrt{t}$ . Then, taking all values of  $n$  and  $m$  for which  $n - \frac{1}{2}m$  and  $n + \frac{1}{2}m$  are both positive integers,

$$\omega_{n,m} = e^{-x} (n + \tfrac{1}{2}m)! \left\{ \frac{1}{m!(n - \tfrac{1}{2}m)!} - \frac{x}{(m+1)!1!(n - \tfrac{1}{2}m - 1)!} \dots \right. \\ \left. + \frac{(-x)^{n-\frac{1}{2}m}}{(n + \tfrac{1}{2}m)!(n - \tfrac{1}{2}m)!} \right\} \\ = (n + \tfrac{1}{2}m)! x^{-\frac{1}{2}m} \cdot \text{coefficient of } h^{n-\frac{1}{2}m} k^{n+\frac{1}{2}m} \text{ in } e^{hk + (k-h)\sqrt{x-z}};$$

or 
$$\sum_{n=0}^{\infty} \sum_{m=-2n}^{m=+2n} x^{\frac{1}{2}m} \omega_{n,m} h^{n-\frac{1}{2}m} k^{n+\frac{1}{2}m} / (n + \tfrac{1}{2}m)! = e^{(h+\sqrt{x})(k-\sqrt{x})}, \quad (34)$$

$n$  taking all half-integer values from 0 to infinity.

Again, taking the same range of values for  $m$  and  $n$ ,

$$\sum \sum x^{\frac{1}{2}m} e^{m i \theta} \omega_{n,m} h^{n-\frac{1}{2}m} k^{n+\frac{1}{2}m} / (n + \tfrac{1}{2}m)! = e^{(h e^{-i\theta} + \sqrt{x})(k e^{i\theta} + \sqrt{x})} = e^{(h+z)(k-z)}. \quad (35)$$

Expanding the last expression by Taylor's theorem, we have

$$x^{\frac{1}{2}m} e^{m i \theta} \omega_{n,m} = (-)^{n+\frac{1}{2}m} (\partial/\partial z)^{n-\frac{1}{2}m} (\partial/\partial z')^{n+\frac{1}{2}m} (e^{-z z'}) / (n - \tfrac{1}{2}m)!$$

Thus, putting  $\xi = re^{i\theta}$  and  $\eta = re^{-i\theta}$ ,

$$x^{\frac{1}{2}m} e^{m i \theta} \omega_{n,m} = (-)^{n+\frac{1}{2}m} 4^{n+\frac{1}{2}} (\partial/\partial \xi)^{n-\frac{1}{2}m} (\partial/\partial \eta)^{n+\frac{1}{2}m} (t^{-1} e^{-\eta^2/4t}) / (n - \tfrac{1}{2}m)!$$

This gives the proof of the relations given above (32).

Putting  $u = p + iq$  and  $-uk = p - iq$  in (35), that expression becomes  $e^{p^2+q^2+(pu+qv)-z}$ , where  $(uv)$  are Cartesian co-ordinates.

Hence

$$(t-t_0)^{-1} e^{-[(u-u_1)^2+(v-v_1)^2]/4(t-t_0)} = (2\pi)^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp dq e^{-(p^2+q^2)(t-t_0)-ip(u-u_1)-iq(v-v_1)} \\ = (2\pi)^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp dq e^{-(p^2+q^2)t - i(pu+qv)} e^{x_1} \sum \sum x_1^{\frac{1}{2}m} e^{m i \phi} \omega_{n,m}(x_1) h^{n-\frac{1}{2}m} k^{n+\frac{1}{2}m} / (n + \tfrac{1}{2}m)!,$$

by (35), where  $x_1 = (u_1^2 + v_1^2)/4t_0$ . Now put  $h' = h\sqrt{(t/t_0)}$  and  $k' = k\sqrt{(t-t_0)}$  and  $h' = p + iq$ ,  $k' = p - iq$ . Then the above becomes

$$\sum \sum (-)^{n-\frac{1}{2}m} (\partial/\partial z)^{n-\frac{1}{2}m} (\partial/\partial z')^{n+\frac{1}{2}m} (2\pi)^{-1} \\ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(p^2+q^2)t - i(pu+qv)} dp dq t_0^{n-\frac{1}{2}m-1} e^{x_1} x_1^{\frac{1}{2}m} e^{m i \phi} \omega_{n,m}(x_1) / (n + \tfrac{1}{2}m)! \\ = \sum \sum (-)^{2n} e^{x_1} x^{-\frac{1}{2}m} x_1^{\frac{1}{2}m} e^{m i (\phi-\theta)} \omega_{n,-m}(x) \omega_{n,m}(x_1) t_0^{n-\frac{1}{2}m-1}.$$

The summation throughout is for all values of  $m$  and  $n$  such that  $n + \frac{1}{2}m$  and  $n - \frac{1}{2}m$  are positive integers. There will thus correspond to each term in the summation another with an equal but opposite value of  $m$ , and, using (17)

these terms will only differ by  $e^{m(\phi-\theta)}$  being changed to  $e^{-m(\phi-\theta)}$ . Remembering also that  $n-\frac{1}{2}m$  is an integer,  $(-)^{-2n} = (-)^{-m}$ . Hence

$$\begin{aligned} & (t-t_0)^{-1} e^{-[(u-u_1)^2 + (v-v_1)^2]/4(t-t_0)} \\ &= \sum_{n=0}^{\infty} e^{x_1 \omega_{n,0}}(x) \omega_{n,0} x_1 t_0^n t^{-n-1} \\ &+ 2 \sum \sum (-)^m e^{x_1 x_1^m x_1^{-1} m} \omega_{n,m}(x) \omega_{n,-m}(x_1) \cos m(\phi-\theta) t_0^n t^{-n-1}. \quad (36) \end{aligned}$$

This expansion is suggestive of Neumann's expansion in the theory of the Bessel function. Another theorem is given below, which, in some respects, is a nearer analogue. The development of the Laplace definite integral follows at once from (36) and is identical with that in the last paragraph (33). The method of this paragraph shows that the values of  $m$  and  $n$  are as there stated.

3. *The Expansion of  $\omega_{m,n}\{(r^2-2rp \cos(\phi-\theta)+\rho^2)/4t\}$  in a Series of  $\omega$ -Functions.*—As in the last section,

$$\begin{aligned} & t^{-1} e^{-[(x-x_1)^2 + (y-y_1)^2]/4t} \\ &= (2\pi)^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp dq e^{-(p^2+q^2)t - ip(u-u_1) - iq(v-v_1)} \\ &= (2\pi)^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp dq e^{-(p^2+q^2)t - ipu - iqv} \\ & \quad \sum \sum (-h)^{n-\frac{1}{2}m} h^{n+\frac{1}{2}m} \eta'^{n-\frac{1}{2}m} \xi^{n+\frac{1}{2}m} / (n-\frac{1}{2}m)! (n+\frac{1}{2}m)! 4^n \\ & \quad \text{(the summation being taken for the same values of } m \text{ and } n \text{ as above)} \\ &= (2\pi)^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp dq (\partial/\partial \xi)^{n-\frac{1}{2}m} (\partial/\partial \eta)^{n+\frac{1}{2}m} e^{-(p^2+q^2)t - ipu - iqv} \\ & \quad \rho^{2n} e^{m(\phi-\theta)} / (n-\frac{1}{2}m)! (n+\frac{1}{2}m)! \\ &= \sum \sum (-)^{n+\frac{1}{2}m} 4^{-n} t^{-n-1} x^{\frac{1}{2}m} \omega_{n,m} e^{m(\phi-\theta)} \rho^{2n} / (n-\frac{1}{2}m)! \\ &= \sum \sum (-)^{n+\frac{1}{2}m} t^{-1} (\rho^2/4t)^{-n} x^{-\frac{1}{2}m} \omega_{n,m}(x) \cos m(\phi-\theta) / (n+\frac{1}{2}m)!, \end{aligned}$$

where the summation extends only to values of  $n$  such that  $n-\frac{1}{2}m$  is a positive integer. Thus  $\omega_{0,0}\{(r^2-2rp \cos(\phi-\theta)+\rho^2)/4t\}$  is expanded in a series of  $\omega$ -functions in the variable  $(r^2/4t)$ , and from this may be derived, by means of relations (32), the expansions of  $\omega_{n,m}\{(r^2-2rp \cos(\phi-\theta)+\rho^2)/4t\}$ , using differentiations with regard to  $t$ ,  $x_1$ , and  $y_1$ .

4. *The Convergence and Validity of the Expansion of a Function in a Series of  $\omega$ -functions.*—The proof of the validity of expansions in a series of normal functions is always a difficult matter, and a general theorem to cover them has yet to be established. A discussion is here given of the expansion in a series of zonal  $\omega$ -functions of a function symmetrical round a point, which seems capable of extension to the general  $\omega$ -functions in a plane without much increase of difficulty, though with considerable addition to the analysis. The multiplication of different discussions for each particular set of normal

functions seems undesirable, however, and the present investigation will therefore be limited to the single case of the zonal functions. A different method appears possible in the discussion of the validity of the processes in the development of the Laplace integral given above.

In the following, the basis of the work is the definite integral expression for the  $\omega$ -function, viz.,  $(2\pi i)^{-1} \int_{\gamma} e^{-x(1+u)} (u+1)^n u^{-n-1} du$ .

The expansion to be justified is

$$f(x) = \sum_0^{\infty} a_r \omega_r(x), \quad \text{where} \quad a_r = \int_0^{\infty} f(y) \omega_r(y) dy.$$

Consider the sum of  $(n+1)$  terms of the series

$$\begin{aligned} \sum_0^n a_r \omega_r(x) &= \sum_0^n \int_0^{\infty} f(y) e^{xy} \omega_r(x) \omega_r(y) dy \\ &= -(4\pi^2)^{-1} \int_0^{\infty} f(y) dy \int_{\gamma} du \int_{\gamma} dv e^{-(u+1)y-(v+1)x} \sum_0^n (u+1)^r (v+1)^r u^{-r-1} v^{-r-1} \\ &= -(4\pi^2)^{-1} \int_0^{\infty} e^{-xy} f(y) dy \int_{\gamma} du \int_{\gamma} dv (u+v+1)^{-1} \\ &\quad \{ (u+1)^{n+1} (v+1)^{n+1} u^{-n-1} v^{-n-1} - 1 \} e^{-xy-vx} = -(4\pi^2)^{-1} \{ I_{n+1} - I_0 \}. \end{aligned}$$

A necessary condition is at once obvious for the validity of the processes involved. For, if  $y$  is very large, since the  $u$ -contour includes points for which the real part of  $u$  is negative,  $e^{-xy}$  is not everywhere finite on that contour. But if  $f(y)$  be such that, no matter how great  $y$  may be,  $f(y) < e^{ky}$ , where  $k$  is some finite negative constant, we may take the  $u$ -contour such that the real part of  $u$  is always greater than  $k$ , and then the integrations required are justified.

Let

$$J_r(x, y) = \int_{\gamma} \int_{\gamma} e^{-xy-vx} (u+1)^r (v+1)^r u^{-r} v^{-r} (u+v+1)^{-1} du dv.$$

Then, if  $y$  is finite,  $J_0$  is zero, since the  $u$ -contour includes no point at which  $(u+v+1)$  vanishes for any value of  $v$  on the contour  $\gamma$ . Also, by the condition assumed to be satisfied by  $f(y)$ , the part of  $I_0$  arising from values of  $y$  greater than a finite magnitude  $\eta$  can be made as small as we please by taking  $\eta$  sufficiently large. Thus  $I_0 = 0$ . In treating  $I_{n+1}$  it has to be remembered that the limit of the integral is sought when  $n$  tends to infinity, and that since the contour  $\gamma$  encircles the point 0, and the two contours for  $u$  and  $v$  have been assumed such that  $u+v+1$  does not vanish for a pair of values within these contours,  $|(u+1)/u|$  and  $|(v+1)/v|$  are both greater

than unity on the major portions of the contours, so that the subject of integration therefore becomes indefinitely great as  $n$  increases.

Consider now the integral  $\int_0^\infty J_r(x, y) dy$  and divide into two portions for which  $y$  is greater and less than  $x$  respectively, calling them  $K_1$  and  $K_2$ .

Let  $K_a$  be the same integral with the limits  $a$  and  $x$  ( $a < x$ ).

Then

$$\begin{aligned} K_a &= \int_a^x dy e^{-x} \int_\gamma du \int_\gamma dv e^{-vx-uy} (u+1)^r (v+1)^r u^{-r} v^{-r} (u+v+1)^{-1} \\ &= - \int_\gamma du \int_\gamma dv e^{-x(1+u+v)} (u+1)^r (v+1)^r u^{-r-1} v^{-r} (u+v+1)^{-1} \\ &\quad + \int_\gamma du \int_\gamma dv e^{-x(1+v)-au} (u+1)^r (v+1)^r u^{-r-1} v^{-r} (u+v+1)^{-1} \\ &= -{}_1K_a + {}_2K_a \text{ (say).} \end{aligned}$$

Consider the latter part  ${}_2K_a$ ; it is absolutely and uniformly convergent, and may therefore be written

$$-\partial/\partial x \int_\gamma \int_\gamma du dv e^{-x(1+v)-au} (u+1)^r (v+1)^{r-1} u^{-r+1} v^{-r} (u+v+1)^{-1} = -\partial L_r / \partial x$$

(say). Within the contours considered there is no pair of points for which  $(u+v+1) = 0$ . If the  $u$ -contour be extended so as to include all the points at which  $(u+v+1)$  vanishes for points on the  $v$ -contour, we add to  $L_r$  the integral  $\int_\gamma \int_{\gamma_1} e^{-x(1+v)-au} (u+1)^r u^{-r-1} (v+1)^{r-1} v^{-r} (u+v+1)^{-1} du dv$ , the contour  $\gamma_1$  including  $u = -v-1$ , but not  $u = 0$ , and this addition

$$= -2\pi i \int_\gamma e^{-(x-a)(1+v)} (1+v)^{-2} dv = 0,$$

since the contour  $\gamma$  does not include the point  $(-1)$ , and since  $x-a$  is positive. Thus the  $u$ -contour in  $L_r$  may be supposed extended so as to include the point at which  $(u+v+1)$  vanishes for all values of  $v$  or  $\gamma$ .

Let the  $v$ -contour be now specified more precisely as that part of a circle of large radius  $R$ , with centre at  $v = -\frac{1}{2}$ , that lies on the positive side of the straight line on which the real part of  $v = -\frac{1}{2}$ , together with that part of this line which lies within that circle. This contour is considered in three parts,  $\alpha, \beta, \gamma$ , as follows:  $\alpha$ , the straight portion;  $\beta$ , that part of the curved portion adjacent to  $\alpha$  and subtending a small angle  $\delta$  at the centre of the circle;  $\gamma$ , the remainder.

For values of  $v$  on  $\alpha$ , the  $u$ -contour, extended to include  $-(1+v)$ , is taken to be a contour just surrounding the complete  $v$ -contour. For values of  $v$  on  $\beta$  and  $\gamma$  this contour is extended in the negative direction so as always

to be a short distance on the negative side of  $u = -v - 1$ . The  $u$ -contour is considered in three portions similar to  $\alpha, \beta, \gamma$ , viz.:  $\alpha_1$ , the straight portion;  $\beta_1$ , the arcs contiguous to  $\alpha_1$  and subtending an angle  $\delta$  at the middle point of  $\alpha_1$ ;  $\gamma_1$ , the remainder. Thus the whole of the double integral is divided into nine portions obtained by combining one of the partial contours  $\alpha, \beta, \gamma$  with one of the partial contours  $\alpha_1, \beta_1, \gamma_1$ .

Now  $e^{-r/v}(1+v^{-1})^r$  remains always finite as  $r$  and  $v$  become large, except for  $v = -1$ , a value which lies outside the region under consideration. Thus  $|e^{-zv}(1+v^{-1})^r| < A|e^{-zv+r/v}|$  and  $|e^{-au}(1+u^{-1})^r| < B|e^{-au+r/u}|$ . Thus, if  $v = Re^{i\phi}|e^{-zv}(1+v^{-1})^r| < Ae^{(-zR+r/R)\cos\phi}$ , and, if  $u = R'e^{i\phi}$ ,  $|e^{-au}(1+u^{-1})^r| < Be^{(-aR'+r/R')\cos\phi}$ . Hence, if

$$r/R'^2 = c < a < x, |e^{-au}(1+u^{-1})^r| < Be^{-(a-c)R'\cos\phi},$$

and therefore, on the arc  $\gamma$ ,  $\cos\phi$  being  $> \delta$ ,

$$|e^{-au}(1+u^{-1})^r| < Be^{-(a-c)R'^2} < Be^{-(a-c)\rho\delta^{-\frac{1}{2}}} \text{ (where } R' = \rho\delta^{-\frac{1}{2}}),$$

and this quantity tends to zero as  $\delta$  diminishes, provided  $\rho$  remains finite.

On the arc  $\beta_1$ , the expression certainly remains finite.

On the straight part  $\alpha_1$ ,  $|(u+1)/u|$  takes its greatest value at the point where it adjoins  $\beta_1$ , i.e.  $\{(u+1)/u\}^r$  is finite on  $\alpha_1$ , but along a length  $(kR')^{\frac{1}{2}}$  of  $\alpha$  measured from the real axis it becomes comparable with  $(1-1/kR')^r$ , i.e. with  $(1-1/kR')^{eR'}$ , i.e. with  $e^{-cR'}$ , where  $R'$  is large and  $c$  finite. Similar considerations apply to the various portions of the  $v$ -contour, and putting them together we deduce that each of the portions of the double integral tends to zero as  $r$  tends to infinity. Thus  $L_{r=\infty}L_r = 0$  for all values of  $x$ , and therefore  $K_a = -\partial L_r/\partial x$  also tends to zero as  $r$  becomes infinite, for any value of  $a$  less than  $x$ , and in particular if  $a = 0$ .

Thus

$$\begin{aligned} K_a &= \int_a^x \int_{\gamma} \int_{\gamma_1} e^{-x(1+v)-uy} (u+1)^r (v+1)^r u^{-r} v^{-r} (u+v+1)^{-1} du dv dy \\ &= - \int_{\gamma} \int_{\gamma_1} e^{-(1+u+v)x} (u+1)^r (v+1)^r u^{-r-1} v^{-r} (u+v+1)^{-1} du dv, \end{aligned}$$

and is independent of the lower limit  $a$ .

The  $u$  and  $v$ -contours being the same, this last integral will be unaltered if  $u$  and  $v$  be interchanged. Hence

$$\begin{aligned} K_a &= -\frac{1}{2} \int_{\gamma} \int_{\gamma_1} e^{-x(1+u+v)} (u+1)^r (v+1)^r u^{-r} v^{-r} (u+v+1)^{-1} (u^{-1}+v^{-1}) du dv \\ &= -\frac{1}{2} \int_{\gamma} \int_{\gamma_1} e^{-x(1+u+v)} (u+1)^r (v+1)^r u^{-r-1} v^{-r-1} \{1-(u+v+1)^{-1}\} du dv \\ &= \frac{1}{2} \{H + \partial H/\partial x\}, \end{aligned}$$

where

$$\begin{aligned} H &= \int_{\gamma} \int_{\gamma_1} e^{-z(1+u+v)} (u+1)^r (v+1)^r u^{-r-1} v^{-r-1} (u+v+1)^{-1} du dv \\ &= - \int_{\gamma} \int_{\gamma_1} e^{-z(1+u+v)} (u+1)^r (v+1)^r u^{-r-1} v^{-r-1} (u+v+1)^{-1} du dv + \epsilon, \end{aligned}$$

where  $\epsilon$  tends to zero as  $r$  becomes large; since, by reasoning similar to that used above, the double integral  $H$  with the  $v$ -contour extended to include the point  $-(1+u)$  vanishes as  $r$  tends to infinity.

Thus

$$Lt_{r=\infty} H = -2\pi i \int_{\gamma} -u^{-1} (u+1)^{-1} du = -4\pi^2 \quad \text{and} \quad Lt_{r=\infty} \partial H / \partial x = 0.$$

Finally, therefore,  $Lt_{r=\infty} K_a = -2\pi^2$ , whatever the value of  $a$ .

Apply now the same treatment to the integral  $K_b$ , viz.:—

$$\begin{aligned} & \int_x^b \int_{\gamma} \int_{\gamma} e^{-z(1+v)-uy} (u+1)^r (v+1)^r u^{-r} v^{-r} (u+v+1) du dv dy \\ &= \int_{\gamma} \int_{\gamma} e^{-z(1+u+v)} (u+1)^r (v+1)^r u^{-r-1} v^{-r} (u+v+1)^{-1} du dv \\ & \quad - \int_{\gamma} \int_{\gamma} e^{-z(1+v)-bu} (u+1)^r (v+1)^r u^{-r-1} v^{-r} (u+v+1)^{-1} du dv. \end{aligned}$$

The coefficient of  $u$  in the exponential in the second integral being now greater than that of  $v$ , we carry out first the integration in regard to  $u$ . The first part of  $K_b$  is, as above, equal to  $2\pi^2$ . Thus

$$K_b = 2\pi^2 - \int_{\gamma} \int_{\gamma} e^{-z(1+v)-bu} (u+1)^r (v+1)^r u^{-r-1} v^{-r} (u+v+1)^{-1} du dv.$$

In extending the  $v$ -contour of this last integral, instead of the  $u$ -contour as in  $K_a$ , we add to it

$$\begin{aligned} & \int_{\gamma} du \int_{\gamma_1} e^{-z(1+v)-bu} (u+1)^r (v+1)^r u^{-r-1} v^{-r} (u+v+1)^{-1} du dv \\ &= 2\pi i \int_{\gamma} du e^{-(b-z)u} / u = -4\pi^2; \end{aligned}$$

$\gamma_1$ , as above, standing for a contour encircling  $-(1+u)$ , and not zero. As before, the extended integral is zero, and therefore the unextended integral equals  $4\pi^2$ . Thus  $K_b = 2\pi^2 - 4\pi^2 = -2\pi^2$  for all values of  $b$ .

We have

$$\begin{aligned} Lt_{r=\infty} \int_0^x f(y) dy \int_{\gamma} \int_{\gamma} e^{-uy-z(1+v)} (u+1)^r (v+1)^r u^{-r} v^{-r} (u+v+1)^{-1} du dv \\ = -2\pi f(x-) \end{aligned}$$



and

$$\text{Lt}_{r=\infty} \int_x^\infty f(y) dy \int_y^\infty e^{-uy-x(1+v)} (u+1)^r (v+1)^r u^{-r} v^{-r} (u+v+1)^{-1} du dv \\ = 2\pi^2 f(x+);$$

and, therefore, finally

$$\text{Lt}_{n=\infty} \sum_0^n a_r \omega_r x = \frac{1}{2} \{f(x-) + f(x+)\},$$

and if the function  $f$  is continuous,

$$\text{Lt}_{n=\infty} \sum_0^n a_r \omega_r (x) = f(x).$$

It will be noticed that the success of the above method depended on the subject of integration in the beginning being a geometrical progression. If the general expansion for the unsymmetrical case (33) is treated similarly, the subject of integration is a double geometrical progression and may be treated similarly, but the analysis will not be carried out here.

#### VII.—*The Application of the $\omega$ -functions in the Theory of Probability.*

1. As was mentioned at the outset, the linear  $\omega$ -functions have been recognised for some time as suitable functions for the purpose of representing a given frequency distribution to any desired degree of approximation. The method commonly adopted in fitting the coefficients is to make the successive moments of the required series equal to those of the given distribution.\* But it does not appear to have been noticed anywhere that this method is exactly equivalent to Hermite's method of obtaining the coefficients. This is an immediate consequence of the fact that the function  $e^{\frac{1}{2}x^2} u_n$  is a polynomial. Thus the practical method by moments, which commonly appears as an artificial way of obtaining a series to represent a distribution of a particular type, is really the exact and unique way of representing an arbitrary function by a series of  $\omega$ -functions. Edgeworth† has another method of obtaining a series of successive approximations to a given distribution in the form  $\exp \left\{ \sum_{r=1}^t k_r (-d/dx)^r / r! \right\} \{ (2\pi k)^{-\frac{1}{2}} e^{-x^2/2k} \}$ , which,

if the formal operator be developed, leads to a series of  $\omega$ -functions. The method of obtaining the coefficients  $k_r$  is that of identifying the moments, so that ultimately the series as obtained by Edgeworth must agree with the direct expansion in  $\omega$ -functions. It might be, however, that, for statistical distributions, the method of development used by Edgeworth would give a

\* Charlier, *loc. cit.*

† 'Camb. Phil. Trans.,' Aug., 1904.

more rapid approximation. The argument as to the magnitudes of the coefficients  $k_r$ , however, appears equally applicable to the present series. It is shown in the memoir quoted that the coefficients  $k_r$  rapidly diminish only if the standard deviation be small. Let this be assumed in forming the series  $a_n u_n(x)$ , where  $u_n = (\partial/\partial x)^n \{ (2\pi\sigma^2)^{-1/2} e^{-x^2/2\sigma^2} \}$ . Then, if  $\mu_n$  be the  $n$ th moment of the distribution, and  $\pi_r = \int_{-\infty}^{\infty} e^{-u^2/2} u^r du$ , we have

$$\mu_n = \sum_0^n (-)^r a_r \sigma^{n-r} \pi_{n-r} n! / (n-r)! (2\pi)^{1/2},$$

and in particular  $\mu_2 = (2\pi)^{-1/2} \{ a_0 \sigma^2 \pi_2 + 2a_2 \pi_0 \}$ ,

and hence, since  $\sigma$  is the standard deviation,  $\pi_2$  is zero. Now, following Edgeworth's argument,  $\mu_n$  is of the order of magnitude  $\sigma^n$ , and hence, by taking the above equations for different values of  $n$ , we see that the coefficient  $a_n$  is of the order  $\sigma^n$ —the word order being used in the same sense as in the work cited. Thus the coefficients  $a_n$  will diminish with about the same rapidity as the quantities  $k_n$ , while the formation of the equations is much simpler.

Pass now to the case of two dimensions. Reference has been made to Hermite's note on the expansion of a function in a series of the form

$$\sum \sum a_{mn} \partial^{m+n} / \partial x^m \partial y^n e^{-1/2 (ax^2 + 2hxy + by^2)},$$

which has been shown to be equivalent to an expansion in  $\omega$ -functions. It is a problem of some importance to obtain a series to represent a frequency distribution in two correlated characteristics, such as, for example, is considered by Perozzo in his memoir on the ages of husband and wife at marriage.\* The lines of equal frequency given by Perozzo are far from being concentric ellipses, as they would be if the frequency surface were a Gaussian normal surface  $z = e^{-1/2 (ax^2 + 2hxy + by^2)}$ . It is therefore worth enquiring whether a few terms of the expansion in  $\omega$ -functions can be made to give an approximation that is tolerably near. The theoretical possibility of representing the distribution by a convergent series is not here considered, though the conditions of validity of the expansion are almost certainly satisfied. Hermite gives a method of obtaining the coefficients. Using the notation

$$\phi(x) = e^{-1/2 (ax^2 + 2hxy + by^2)}, \quad \psi(x) = e^{-1/2 (bx^2 - 2hxy + ay^2)},$$

$$(\partial/\partial x)^m (\partial/\partial y)^n \phi = \phi \cdot U_{m,n}, \quad (\partial/\partial x)^m (\partial/\partial y)^n \psi = \psi V_{m,n},$$

$U_{m,n}$  and  $V_{m,n}$  are both polynomials of degrees  $(m+n)$  in  $x$  and  $y$ . If  $f(x, y)$  be expanded in the form  $\sum \sum a_{mn} \phi U_{m,n}$ , it is proved that

$$a_{m,n} = a_{m,n} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(xy) V_{m,n} dx dy,$$

\* 'Annali di Statistica,' 1883.

where  $a_{m,n}$  is a numerical constant depending on  $m$  and  $n$  alone. Now it will be much more convenient in practice to obtain the coefficients by means of equating the successive moments  $\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y) x^m y^n dx dy$  to the corresponding moments of the series. This is equivalent to Hermite's process,  $V_{m,n}$  being a polynomial; so that  $a_{m,n}$  above is a linear function of the moments.

Putting  $u_{rs} = \phi U_{rs}$ ,  $\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u_{rs} x^m y^n dx dy$  can be reduced by successive integrations by parts. If  $m < r$ , we have

$$\int \int u_{rs} x^m y^n dx dy = (-)^m m! \int \int y^n u_{r-m, s} dx dy = 0,$$

whatever the values of  $s$  and  $n$ , and, similarly, the integral is zero if  $n < s$ , whatever the values of  $r$  and  $m$ . But if  $m = r$ , and  $n = s$ ,

$$\int \int u_{rs} x^m y^n dx dy = (-)^{m+n} m! n! \int \int \phi dx dy,$$

and if  $m > r$  and  $n > s$ ,

$$\int \int u_{rs} x^m y^n dx dy = (-)^{r+s} (m!/(m-r)!) (n!/(n-s)!) \int \int \phi x^{m-r} y^{n-s} dx dy,$$

and this last integral is again zero if  $m-r+n-s$  is an odd integer.

Using the notation  $\phi_{rs} = \int \int \phi x^r y^s dx dy$  and  $\mu_{rs} = \int \int f x^r y^s dx dy$ , if we multiply the equation  $f(x, y) = \sum a_{rs} u_{rs}$  by  $x^r y^s$  and integrate, we have

$$\begin{aligned} \mu_{rs} &= a_{00} \phi_{rs} - (r a_{10} \phi_{r-1, s} + s a_{01} \phi_{r, s-1}) \\ &\quad + \{r(r-1) a_{20} \phi_{r-2, s} + r \cdot s a_{11} \phi_{r-1, s-1} + s(s-1) a_{02} \phi_{r, s-2}\} \dots, \end{aligned}$$

there being  $(r+1)(s+1)$  terms on the right, of which those are zero in which the sum of the subscripts of  $\phi$  is odd.

Taking the first few equations, by choosing the origin at the mean of the distribution, and choosing the constants  $a, b, h$  so that

$$\mu_{20} : \mu_{11} : \mu_{02} : \mu_{00} = \phi_{20} : \phi_{11} : \phi_{02} : \phi_{00},$$

the constants  $a_{01}, a_{10}, a_{20}, a_{11}, a_{02}$  all become zero. By this means the normal surface that best fits the distribution is obtained, viz.,  $\mu_{00} \phi / \phi_{00}$ .

But the fact that the contour lines in the example quoted are by no means concentric ellipses with centre at the mean shows that the fit is not yet sufficiently good.

The next approximation to the distribution is

$$\mu_{00} \phi / \phi_{00} + (\mu_{20} u_{20} + 3 \mu_{21} u_{21} + 3 \mu_{12} u_{12} + \mu_{03} u_{03}) / 6 \phi_{00}.$$

The equations giving the coefficients of the fourth order terms are :

$$\mu_{40} = a_{00}\phi_{40} + 4!a_{40}\phi_{00}\mu_{31} = a_{00}\phi_{31} + 3!a_{31}\phi_{00}, \quad \mu_{22} = a_{00}\phi_{22} + 2!2!a_{22}\phi_{00}, \text{ etc.}$$

Thus in terms of the moments  $\mu_{rs}$  the coefficients are quickly obtained, and Edgeworth's argument as to the rapidity of approximation applies equally well here if the standard deviations are sufficiently small. But the labour of obtaining the moments is very great, and a suitable example for testing the closeness of approximation is not available. What will be done here, therefore, is to show more or less generally how, in a simple case, contour lines can be obtained which are approximately of the type found in the example given above (see diagrams, Perozzo, *loc. cit.*).

2. *An Example of Contour Lines in Two Dimensions.*—The example chosen here is that of  $\phi = e^{-\frac{1}{2}(x^2 + y^2)}$ , and it will be assumed that there is symmetry about the line  $x = y$ .

The most general first correction is  $\alpha(u_{30} + u_{03}) + \beta(u_{21} + u_{12})$ , where  $u_{30} = \phi(3x - x^3)$ ,  $u_{21} = \phi y(1 - x^2)$ ,  $u_{12} = \phi x(1 - y^2)$ ,  $u_{03} = \phi(3y - y^3)$ .

In particular, if  $\beta = 0$ , and  $\alpha$  is negative,  $\alpha(u_{30} + u_{03})$  vanishes on the straight line  $x + y = 0$ , and the ellipse  $x^2 - xy + y^2 = 3$ ; on the positive side of  $x + y = 0$  it is positive outside the ellipse, and negative inside, and *vice versa* on the negative side of  $x + y = 0$ .

Thus the effect of the correction  $\alpha(u_{30} + u_{03})$ , while not altering the mean or second moments, is to introduce *skewness* about  $x + y = 0$ , the maximum ordinate being displaced in the negative direction along  $x = y$ . Outside the ellipse  $x^2 - xy + y^2 = 3$  the surface is depressed on the negative side of  $x + y = 0$ , and raised on the positive side. The zero-line of  $\phi + \alpha(u_{30} + u_{03})$  is shown in the figure (curve A) for  $\alpha = -1/10$ .

The contour lines on the positive part of the surface will now be oval curves surrounding the point of maximum ordinate with their greatest width parallel to  $x + y$ , and crowding closely together in the neighbourhood of the zero-curve. These have not been shown in the figure to avoid complication. A variation in their form could be produced by introducing a term  $\beta(u_{12} + u_{21})$ , but the effect of skewness is again the most noticeable.

Consider now a fourth order correction, which for the end in view has been conveniently taken to be

$$\gamma(u_{22} - u_{21} - u_{12}) = \gamma\{1 - x^2 - y^2 + 6xy - xy(x^2 - xy + y^2)\}.$$

The curve for which this is zero is drawn in the figure (curve B), and the portions of the plane are indicated in which it is positive and negative respectively. Thus the effect of this correction on the contour lines in the neighbourhood of the maximum ordinate is to contract them in the direction

$x = -y$ , and to elongate them in the direction  $x = y$ . A series of contour lines is drawn for  $\gamma = 1/20$ ; so that the lines shown are curves of equal frequency for the function

$$\{1 - \frac{1}{10}(\partial^3/\partial x^3 + \partial^3/\partial y^3) + \frac{1}{10}(\partial^4/\partial x^2\partial y^2 - \partial^4/\partial x\partial y^3 - \partial^4/\partial y\partial x^3)\}e^{-\frac{1}{2}(x^2+y^2)}.$$

The curves are distinctly similar in type to Perozzo's curves, though no attempt has been made at determining exactly what the coefficients should be. Probably a better approximation would be found with a rather larger coefficient for the third order correction, as the skewness is not so marked as it should be.

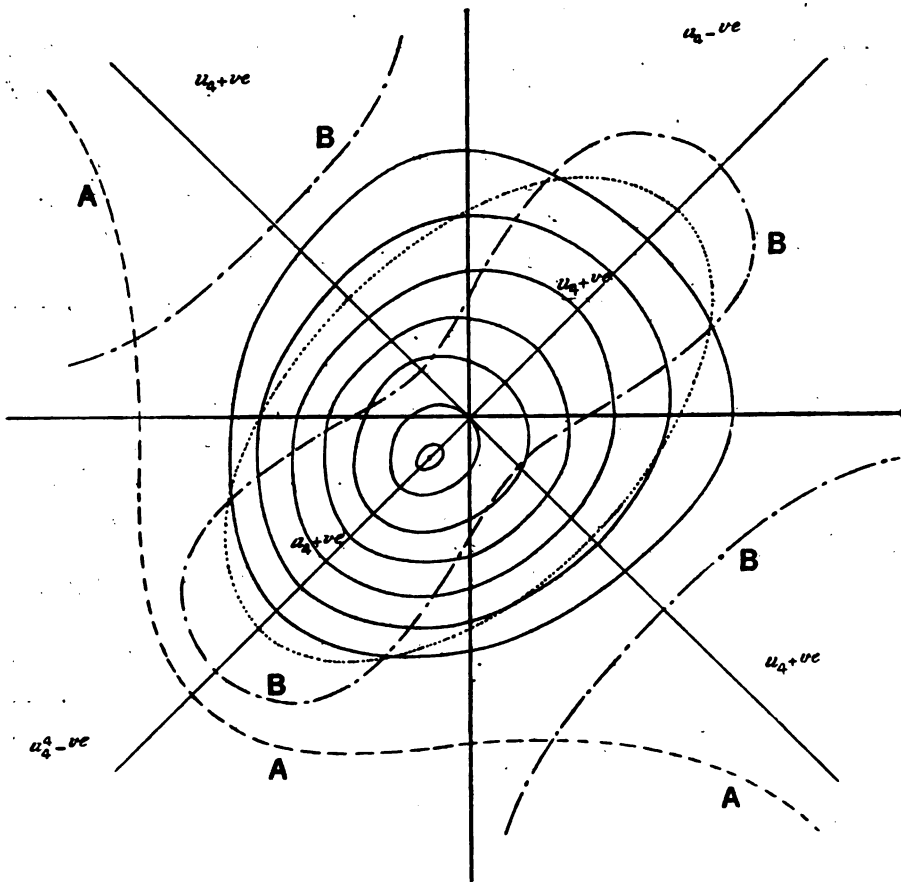


Figure showing Contour Lines of the Surface

$$z = \{1 - \frac{1}{10}(\partial^3/\partial x^3 + \partial^3/\partial y^3) + \frac{1}{10}(\partial^4/\partial x^2\partial y^2 - \partial^4/\partial x\partial y^3 - \partial^4/\partial y\partial x^3)\}e^{-\frac{1}{2}(x^2+y^2)}.$$

**A**—the curve  $\{1 - \frac{1}{10}(\partial^3/\partial x^3 + \partial^3/\partial y^3)\}e^{-\frac{1}{2}(x^2+y^2)} = 0$ .

**B**—the curve  $u_4 = \{\partial^4/\partial x^2\partial y^2 - \partial^4/\partial x\partial y^3 - \partial^4/\partial y\partial x^3\}e^{-\frac{1}{2}(x^2+y^2)} = 0$ .

Similar curves can clearly be obtained where there is correlation to be taken into account. For by making the change of variable

$$\xi - \eta = \alpha(x - y), \quad \xi + \eta = \beta(x + y), \quad e^{-\frac{1}{2}(\alpha^2 + \beta^2)}$$

is turned into a normal surface with correlation, while  $\partial/\partial x$  and  $\partial/\partial y$  are linear functions of  $\partial/\partial \xi$  and  $\partial/\partial \eta$ .

*Eutectic Research.* No. 1.—*The Alloys of Lead and Tin.*

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(Communicated by Dr. R. T. Glazebrook, F.R.S. Received June 17,—Read June 25, 1908.)

(From the National Physical Laboratory.)

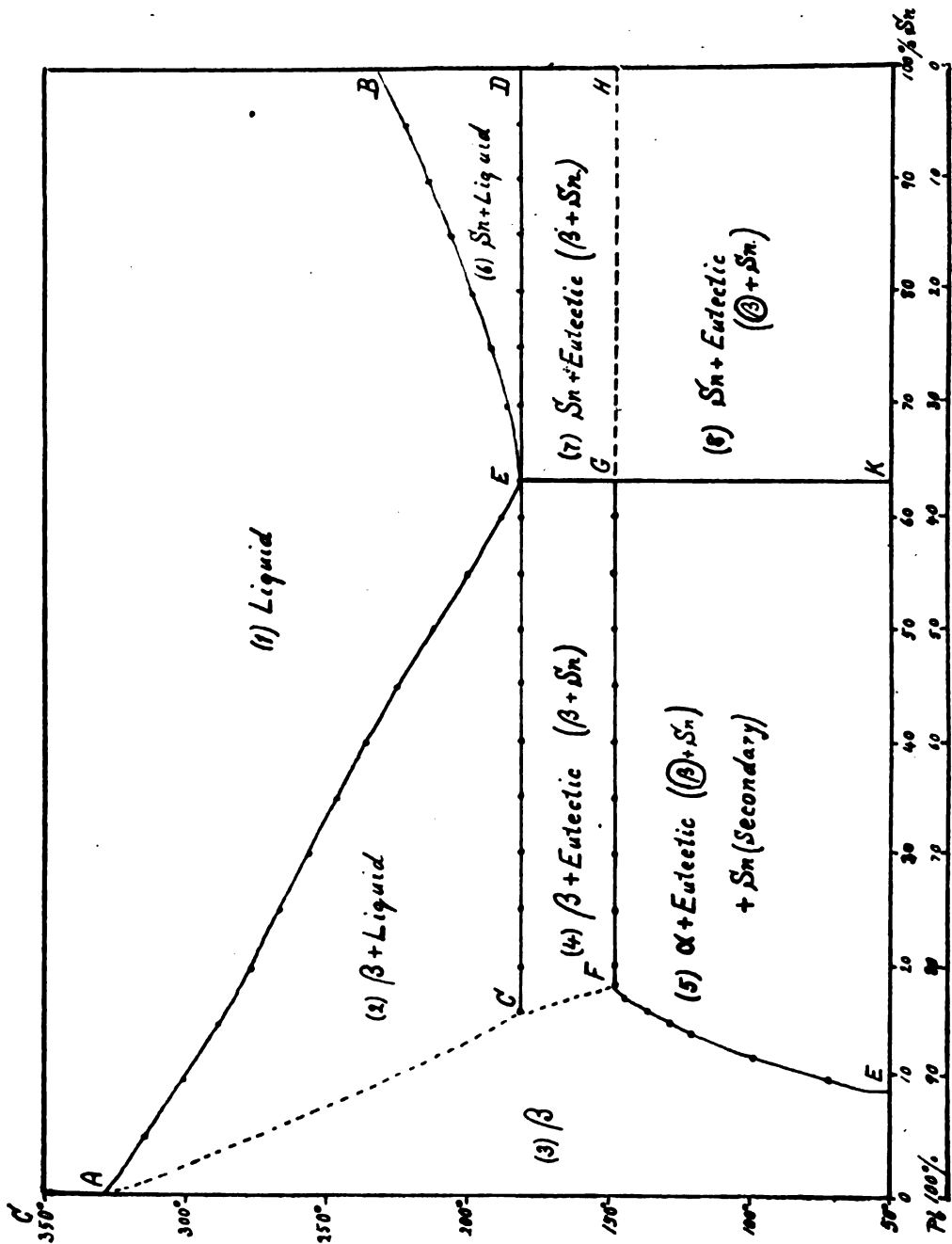
(Abstract.)

Attempts to prepare pure eutectic alloys of known constitution led to the discovery of discrepancies between the authors' experiments and the data on lead-tin alloys published by Roberts-Austen. A complete redetermination of the equilibria of the lead-tin system was therefore undertaken, by both pyrometric and microscopical methods. Cooling-curves of the alloys taken by both inverse-rate and differential methods are given; these, together with the microscopic data, lead to the equilibrium diagram shown in the figure. This differs principally from that given by Roberts-Austen,\* in that the eutectic point is placed at a concentration of 63 per cent. of tin instead of 69, that the eutectic line towards the lead end of the series terminates at a concentration close to 16 per cent. of tin, and that a series of transformations (along the line EFG) have been found in the solid alloys near the lead end of the series.

The discrepancies of these results, as regards the eutectic composition, arise from the more delicate method employed in the present research. While alloys within 1 per cent. on either side of the true eutectic composition show no detectable difference in freezing- or melting-point, the presence of small amounts of excess of either constituent can be detected by the microscope, and in this manner the composition of the pure eutectic has been ascertained. As regards the solubility of tin in solid lead, it was found that the occurrence of the eutectic arrest-point in alloys containing less than 16 per cent. of tin

\* Roberts-Austen, 'Fifth Report to the Alloys Research Committee of the Institution of Mechanical Engineers,' 1897.

depended upon the rate of cooling; by maintaining alloys at a temperature of  $175^{\circ}\text{C}$ . for periods up to six weeks, approximately complete equilibrium conditions can be attained, and the study of the cooling-curves and micro-



structure of such alloys has led to the conclusions embodied in the diagram. These conclusions are much strengthened by the fact that the authors have succeeded in preparing alloys very rich in lead for microscopic examination by polishing with levigated oxide of chromium.

The transformation in the solid alloys along the line of the diagram has also been studied by means of cooling-curves of alloys, both when cooled direct from fusion and after prolonged heating at 175° C.; a rough quantitative interpretation of the indications of these cooling-curves is given on the lines laid down in a recent paper on this subject.\* The changes in micro-structure associated with this transformation have also been studied, and for this purpose specimens of the alloys, after prolonged heating, were quenched in liquid air from a temperature just above that of the transformation, and their structure was compared with that of specimens quenched in liquid air from temperatures just below the transformation point and also with others cooled very gradually to the ordinary temperature. The conclusion arrived at is that the transformation involves the rejection of tin from the solid solution of tin in lead. The evidence does not support the view that the formation of a definite compound is involved, but indicates that the change takes place in the solid solution of tin in lead which passes from one modification ( $\beta$ ) to another ( $\alpha$ ) on cooling. The reversal of this change is very gradual when the alloy is heated above the transformation temperature. In the case of alloys containing less than 16 per cent. of tin, the transformation occurs at lower temperatures in the alloys containing least tin; thus while the 16-per-cent. alloy undergoes the change on cooling to 159° C., the alloy with 8 per cent. of tin passes through the change only when cooled to 72° C. For still lower concentrations of tin the change could not be observed, even when cooling-curves down to the temperature of liquid air were taken, thus proving that the change in question is not simply due to allotropy in lead, but that the presence of tin is essential to its occurrence. A further curious feature in connection with this change is that the lead-rich constituent of the eutectic does not take part in the transformation, and must therefore be regarded as retaining the  $\beta$  condition in the metastable form. The non-transmission of the reaction from the free lead-rich constituent to that forming part of the eutectic is readily explained from the micro-structure of the alloys, which always show the crystallites of this constituent surrounded by a sheath of pure tin, thus separating it mechanically from the lead-rich constituent of the eutectic.

The chemical composition and constitution of the eutectic is deduced from

\* W. Rosenhain, 'Observations on Recalescence Curves,' Physical Society of London, January 24, 1908.



the equilibrium diagram, and its density as determined by the authors is compared with that of its two constituent phases; there is a discrepancy which is ascribed to the persistence of meta-stable  $\beta$  in the eutectic; this difference of density, as found from the density of the eutectic, and as determined directly, amounts to 0.08, which is too large a difference to be ascribed to experimental error. The volume composition of the eutectic is calculated and found to be 1.8 volumes of tin to 1 volume of the lead-rich  $\beta$  body; this indicates the great extent to which the tin is the predominating constituent of the eutectic.

The structure of numerous examples of the lead-tin eutectic is described and illustrated by a number of photo-micrographs; the eutectic is found to consist of regions or grains, in each of which there is a systematic orientation of the laminations produced by layers of the two constituents. Study of typical examples under oblique illumination and low magnification leads to the view that these grains are true spherulitic crystals, *i.e.* crystals having a regular radiating structure, and it is suggested that this structure is due to the manner in which the predominating constituent has crystallised, leaving the other constituent to fill up the interstices between the radiating dendrites formed by the first. The microscopic features, at all events, preclude the view that the eutectic is an indiscriminate mixture of separate minute crystals of each of the two phases.

Finally, the authors describe some eutectic and other lead-tin alloys prepared by compression of powders of the constituent metals, and give photo-micrographs proving that the original particles persist unchanged in alloys prepared in this way, *i.e.* that there is no real flow or diffusion, at all events in the relatively short time for which these alloys have so far been under observation, even at temperatures up to the melting-point of the eutectic.

The authors express their indebtedness to Dr. R. T. Glazebrook, F.R.S., and to members of the staff of the laboratory in connection with the work described in the paper.

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*The Spectrum of Scandium and its Relation to Solar Spectra.*

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Read June 25, 1908.)

## (Abstract.)

The greater part of this investigation of the spectrum of scandium under different experimental conditions has been based on purified scandia, generously placed at the author's disposal by Sir William Crookes. The principal results are as follows:—

1. The arc spectrum of scandium consists of two distinct sets of lines, which behave very differently in solar spectra. Each set includes both strong and faint lines.

2. Lines belonging to one set correspond with the enhanced lines of other elements, notwithstanding that they appear strongly in the ordinary arc spectrum—

- (a) These lines are very feeble or missing from the arc-flame spectrum, and are strengthened in passing to the arc, the arc in hydrogen, or the spark.
- (b) They occur as relatively strong lines in the Fraunhofer spectrum.
- (c) They are weakened in the sun-spot spectrum.
- (d) They occur as high-level lines in the chromosphere.

3. The remaining lines show a great contrast when compared with the first group—

- (a) They are relatively strong lines in the arc-flame.
- (b) They are very feebly represented in the Fraunhofer spectrum.
- (c) The stronger lines are prominent in the sun-spot spectrum.
- (d) They have not been recorded in the spectrum of the chromosphere.

4. The special development of the enhanced lines in the Fraunhofer spectrum, together with their presence in the upper chromosphere, indicates that the greater part of the scandium absorption in the solar spectrum originates at a higher level than that at which the greater part of the iron absorption is produced.

5. The discussion of scandium lines indicates that while in the case of some elements solar identifications are to be based chiefly on arc lines, in

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others it is the enhanced lines which may be expected to show the most important coincidences.

6. The flutings which occur in the arc and arc-flame do not appear when the arc is passed in an atmosphere of hydrogen. As suggested by Thalén, they are probably due to oxide of scandium.

Tables are given which show the lines of the arc spectrum from 3930 to 6580, the positions of the oxide flutings, and comparisons of the principal lines of the two classes with the sun, sun-spots, and chromosphere.

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### *On the Vapour-pressure and Osmotic Pressure of a Volatile Solute.*

By H. L. CALLENDAR, M.A., F.R.S., Professor of Physics at the Imperial College of Science and Technology.

(Received June 17,—Read June 25, 1908.)

It follows by a method given in a recent paper by the author that if the osmotic membrane be assumed to be impermeable to the solute, the formula for the change of vapour-pressure of a volatile solute with hydrostatic pressure, and also the formula for the osmotic pressure which is deduced from it, must be the same as the formula for a non-volatile solute, and should not contain any terms depending on the vapour-pressure of the solute, except in so far as it may affect the hydrostatic pressure of the solution.

If, on the other hand, an osmotic membrane is regarded as a vapour-sieve, permeable to the vapour of the solution but not to the liquid phase, the equation takes a different form, depending on the concentration of the constituents in the vapour-phase. If  $c_1, c_2$ , etc., be the concentrations of the constituents in grammes per gramme of the vapour, and if  $U_1, U_2$ , etc., be the specific volumes of the constituents in the solution, the change of total vapour-pressure  $dp$  of the solution for a change of hydrostatic pressure  $dP$  is given by the relation,

$$\sum cU dP = v dp,$$

where  $v$  is the specific volume of the whole vapour-phase. If only one constituent is volatile, this relation reduces to the form  $U dP = v dp$  for that constituent.

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*The Emission and Transmission of Röntgen Rays.*

By G. W. C. KAYE, B.A. (Cantab.), B.Sc. (Lond.), A.R.C.Sc., Trinity College, Cambridge.

(Communicated by Professor J. J. Thomson, F.R.S. Received June 17,—  
Read June 25, 1908.)

(Abstract.)

A Röntgen ray tube was designed with an anticathode which consisted of a number of elements mounted on a small car. By means of an external magnet the car could be moved, and any element desired brought under the beam of cathode rays. The Röntgen rays produced (by a coil discharge) passed out through a thin aluminium window, and their intensity was measured by an ionisation method. Some twenty elements were used as anticathodes, and the effects upon their radiations of a number of different metal screens were investigated.

The results of the work give rise to the following conclusions:—

1. The relative intensities of the radiations as they issue from the window of the tube, unobstructed by any screen, do not follow the order of the atomic weights of the anticathodes. The order shows agreement with that given by Starke for the relative numbers of cathode rays returned by metallic reflectors. The intensities indicate a grouping of the elements which agrees with, and in features is similar to, that arrived at by Barkla and Sadler from a consideration of the secondary Röntgen rays.

2. Over a certain region, when screen and radiator are of the same metal, selective transmission of the radiation is manifested, that is, the radiation from the metal is augmented relative to the radiations from other anticathodes. The effect is also present to a less extent when radiator and screen have closely adjoining atomic weights.

3. This augmentation, when radiator and screen are alike, is most pronounced in the case of the metals of the chromium-zinc group. It is least marked for a substance of low atomic weight such as aluminium, which of the metals tried can be regarded as the most suitable for screens to measure ray intensities.

4. Generally speaking, the lower the atomic weight of a metal in a group the softer is the radiation for which it shows special transparency.

5. If the different radiations are cut down by aluminium screens of increasing thickness, the intensities reach ultimate relative values which are not altered by a further increase in the thickness of the screen. These intensities when plotted against the atomic weights of the radiators yield,

roughly speaking, a straight line. The relative values of the heavy-atom metals increase somewhat with a rise in potential on the tube. There is reason to believe that screens of other metals would eventually yield much the same sort of curve, modified slightly in the neighbourhood of the atomic weight of the radiator.

6. When screen and radiator are alike, the absorption per unit mass of unit area of the screen ( $\lambda/\rho$ ) is relatively low. One of the consequences of this is that the shape of Benoist's "transparency" curve, besides depending on the range and degree of absorption, is largely dependent on the material of the anticathode. For example, the curve is much straighter for a radiator of aluminium than for one of platinum working under the same conditions. With an anticathode belonging to the chromium-zinc group the transparency curve has to be modified by the addition of a sharp maximum in the neighbourhood of the radiator. Barkla and Sadler have obtained a similar result in the case of secondary Röntgen rays.

7. The question of the atomic weight of nickel is gone into, and an explanation put forward to account for the anomalous results obtained with the secondary radiation from this element.

8. The curve of transmission in which the thickness of screen is plotted as abscissa against the logarithm of the intensity consists, in general, of three parts when radiator and screen are of the same metal. First with thin screens there is a relatively steep portion, which for thicker screens is followed by a straight-line region; this again is ultimately succeeded by one in which the slope gradually diminishes with the thickness of the screen. Corresponding to the straight-line portion of the curve there is, of course, an exponential absorption. The extent of this region diminishes with the potential on the tube. The preliminary steepness is attributed to secondary radiation; the extent of the steepening for each metal agrees with that obtained by McClelland working with the  $\beta$ -rays of radium. The ultimate flattening of the curve is probably due both to scattering and to the presence of hard primary rays. This latter region may not be detectable if the potential on the tube is not too high; the absorption curve then indicates homogeneity throughout its length.

9. When screen and radiator have very different atomic weights, the region of exponential absorption does not appear. The early portion of the logarithmic curve is steepened by secondary radiation, but throughout the whole region the transmission is one in which the coefficient of absorption steadily diminishes as the thickness of screen increases. This result is brought about in the early stages chiefly by scattering, and in the later stages by the heterogeneity of the primary beam of rays.

*The Boiling-point of Sulphur on the Constant-pressure  
Air Thermometer.*

By N. EUMORFOPOULOS, B.Sc., Assistant in the Department of Physics,  
University College, London.

(Communicated by Professor H. L. Callendar, F.R.S. Received June 19,—  
Read June 25, 1908.)

The following experiments were undertaken at the suggestion of Professor Callendar, with a view to the redetermination of the boiling-point of sulphur (S.B.P.) on the scale of the constant-pressure air thermometer. The experiments unfortunately have not led to a result that can be regarded as final, owing to the uncertainty in the expansion of the glass, but it has been thought desirable to publish the results.\*

The air thermometer was made of Jena glass, 16 III, and is in construction substantially the same as that described by Callendar.† Fig. 1 will make clear the form of the apparatus, and is drawn roughly to scale.

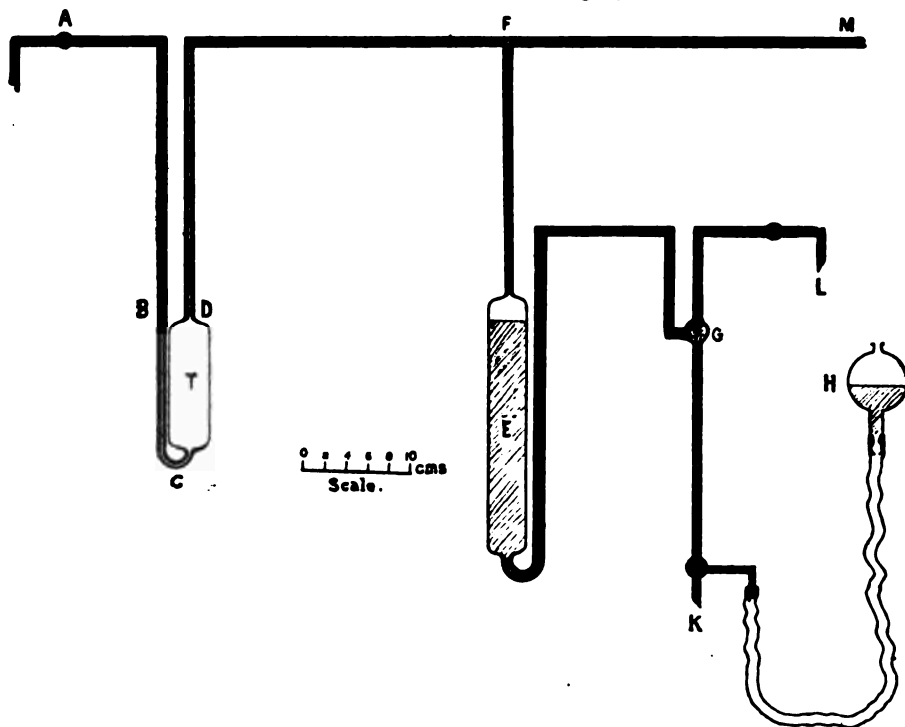


FIG. 1.

\* All measurements of length are given in centimetres, and all measurements of volume in grammes of mercury at 0° C.

† H. L. Callendar, 'Roy. Soc. Proc.,' vol. 50, p. 247; 'Ency. Brit.,' "Thermometry."

T is the bulb to be heated, and is connected by capillary tubes on the one side to a tap A, and on the other to a second bulb E and by M to the gauges, which will be described shortly; E itself is connected to an inlet for mercury at L and an outlet at K. The reservoir H is convenient in setting up the apparatus, but is not used in the actual experiments. There is a small air-trap at G, in case air is accidentally introduced in manipulation through

K or L. This part of the apparatus which contains the bulb T may be termed the thermometric side (T side).

Alongside the above, and quite close to it, is an exactly similar system of tubes, except that the bulb T is missing, so that the capillary tube passes straight across from D to B (instead of down to C), and thence to a stopcock alongside A. This second system can be called the compensation side (C side), and contains a bulb similar to, and alongside, E.

The two systems are connected together by the gauges, which are represented in fig. 2. NOP is a mercury gauge for the rough adjustment of the pressure, while NQP is an oil gauge for the fine adjustment. O and Q are three-way stopcocks. It should be added that the plane of fig. 2 is at right angles to that of fig. 1.

In an actual experiment the air in T is limited in the direction of A by a thread of mercury which occupies part of the horizontal tube, in the direction of the gauges by the mercury and oil they contain, while E, which

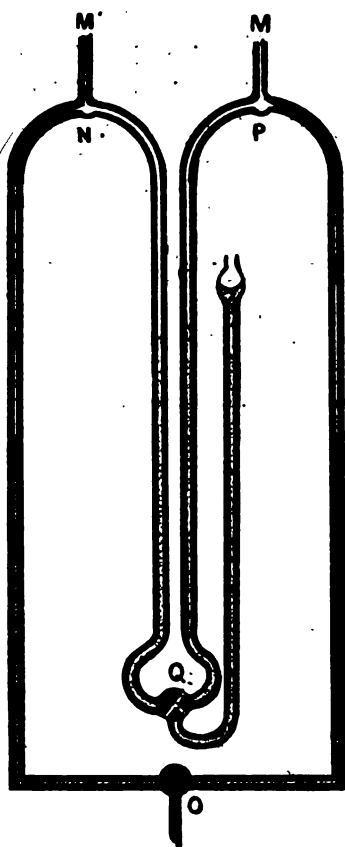


FIG. 2.

is always immersed in ice along with the corresponding bulb on the C side, contains a variable amount of mercury; the latter occupies also the capillary tubes to the outlets at H, K, and L. It is by varying the amount of mercury in E that the pressure on the T side is always adjusted to a certain standard, this standard being the pressure of the air on the C side in the bulb corresponding to E. It is thus unnecessary to read the barometer for this purpose. The mass of air on the C side is made as nearly as possible equal to that on the T side. If now the capillary tubes on the two sides are of the same temperature and volume at corresponding points, they exactly compensate

one another, as will be shown later. As, however, it is impossible to make the volumes absolutely equal, a rough measurement of the temperature is all that is necessary.

It will be noted that there is either mercury or oil at all the stopcocks; they are thus not assumed to be gas-tight. The diameter of all the connecting tubes is approximately 0.1, except that of the oil-gauge, which is 0.2. The latter was read by means of a microscope containing in the eye-piece a scale divided to 0.01; differences of pressure were thus read to 0.001 cm. of oil such as is used in a Fleuss pump. The weighings were made to the nearest milligramme. In order to ensure the delivery of mercury being accurate to this, the open end of each delivery tube was slightly constricted, the tube cut off at 45° to the axis at the narrowest part, and the end ground. The concordance of the results obtained when determining the expansion of the glass indicates that the delivery of mercury is probably accurate to 1 milligramme (1 in 360,000 on the F.I.).

It has already been stated that the oil in the oil gauge was that used in a Fleuss pump. The fact that it can be so used indicates that its vapour-pressure must be very low. For additional security a flask containing a sample of this oil was heated to 100° C. and kept evacuated for some time to remove any lower boiling substance that might be present. In this operation it was found that the oil dissolves a very small, though appreciable, quantity of air. The density of this sample was determined at 10° C. and at 20° C.

#### *Development of Formula.*

In the course of an experiment the two bulbs E are always kept at 0° C., or  $T_0$  absolute. The bulb T is heated to any required temperature T. No change whatever is made on the C side, but on the T side mercury is added or removed, until the pressures on the two sides are as nearly as possible equal, any residual difference being read on the oil gauge by the microscope already referred to.

*C side.*—

Let the volume of gas in the bulb E = S, this at temperature  $T_0$  (absolute),

“ “ connecting tubes =  $v$ , “ “  $\theta$  “

then 
$$\frac{S}{T_0} + \frac{v}{\theta} = \frac{mR}{p},$$

where  $m$  = mass of gas and  $p$  its pressure, R being the usual gas constant.

*T side.*—

Let the volume of gas in the bulb T = V at temperature T (absolute),

“ “ “ E = Q “  $T_0$  “

“ “ connecting tubes =  $v + \delta v$  “  $\theta$  “



Let the mass of the gas =  $m + \delta m$ , and its pressure =  $p + \delta p$ ,

$$\text{then} \quad \frac{V}{T} + \frac{v + \delta v}{\theta} + \frac{Q}{T_0} = \frac{m + \delta m}{p + \delta p} R = \frac{mR}{p} \left( 1 + \frac{\delta m}{m} - \frac{\delta p}{p} \right)$$

approximately, as  $\delta m$  and  $\delta p$  are very small quantities.

Subtracting the former expression from the latter, we get

$$\frac{V}{T} = \frac{S - Q}{T_0} + \frac{R}{p} \delta m - \frac{mR}{p^2} \delta p - \frac{\delta v}{\theta}.$$

When obtaining the freezing-point of water (W.F.P.), the bulb  $T$  is surrounded by ice. Let us call the corresponding quantities  $\delta p_0$ ,  $\delta v_0$ ,  $\theta_0$  (note that the latter is not  $0^\circ \text{C.}$ ). Then, as  $p$  remains practically constant,

$$\frac{V_0}{T_0} = \frac{S_0 - Q_0}{T_0} + \frac{R}{p} \delta m - \frac{mR}{p^2} \delta p_0 - \frac{\delta v_0}{\theta_0}.$$

We thus obtain the following equation :

$$\frac{V}{T} = \frac{V_0}{T_0} - \frac{Q - Q_0}{T_0} + \frac{S - S_0}{T_0} + \frac{mR}{p^2} (\delta p_0 - \delta p) + \frac{\delta v_0}{\theta_0} - \frac{\delta v}{\theta}.$$

It will be noticed that the term involving  $\delta m$  has disappeared from this equation. It is necessary, however, that  $\delta m$  should be small, otherwise the compensation will be inaccurate.

Multiply throughout by  $\rho$ , the density of mercury at  $0^\circ \text{C.}$ , so as to convert volumes into weights of mercury; we thus get, with an easily understood notation,

$$\frac{W}{T} = \frac{W_0}{T_0} - \frac{w}{T_0} + \frac{(S - S_0)\rho}{T_0} + \frac{mR\rho}{p^2} (\delta p_0 - \delta p) + \left( \frac{\rho \delta v_0}{\theta_0} - \frac{\rho \delta v}{\theta} \right).$$

Writing this equation, for shortness, in the form

$$\frac{W}{T} = \frac{W_0}{T_0} - \frac{w}{T_0} + A + B + C,$$

we have finally

$$\frac{t}{T_0} = \frac{(W - W_0) + w - (A + B + C) T_0}{W_0 - w + (A + B + C) T_0},$$

where  $t \equiv T - T_0$ , and is the temperature on the scale of this gas thermometer.

To obtain the coefficient of expansion of the gas, or its reciprocal  $T_0$ , after observing the W.F.P., the bulb  $T$  is surrounded with steam, thus giving the boiling-point of water (W.B.P.).  $t$  is thus approximately 100, while the right-hand side of the equation contains known quantities. We can hence calculate  $T_0$ . In obtaining the S.B.P. the converse of this process is gone through,  $T_0$  being now known, while  $t$  is calculated.

The volumes of the connecting tubes, etc., were obtained by finding the quantity of mercury required to fill them. When the weight exceeded a few

grammes, weighings were made in both pans, and a buoyancy correction applied.

The following remarks will indicate the corrections that have been applied to the various terms of the above equation :—

(i)  $W_0$ .—This depends slightly on the height to which the ice is piled, as the two sets of tubes do not exactly compensate one another.

(ii)  $W$ .—Besides the correction mentioned in (i), allowance has to be made for the expansion of the glass. This will be discussed later.

There may be a small pressure correction to apply to  $W_0$  and  $W$  owing to variations of the *external* pressure. This, however, never amounts to more than 2 or 3 milligrammes.

(iii)  $w$ .—The weight of the mercury in E causes this bulb to expand. As, therefore, mercury is removed, the bulb contracts. The correction due to this pressure effect amounts to 4 milligrammes for the W.B.P., and to 8 for the S.B.P. There is no external pressure correction, as this effect is compensated.

(iv)  $A$ .—As the two air-traps G (of fig. 1) are not exactly of the same volume, S may on this account differ from  $S_0$ . This correction is, however, quite small, a change of temperature of  $10^\circ$  being equivalent to 6 milligrammes.

(v)  $B$ .—This does not call for any remark.

(vi)  $C$ .—This term depends on imperfect compensation of the tubes connecting together the various parts of the apparatus. The temperature was read at three points: one thermometer was placed just above BD (of fig. 1), another just above this at the bend, and a third between N and P (of fig. 2). The reason for this distribution is obvious. The first thermometer would be considerably affected by the heating of T, the second to a much smaller extent, and the third scarcely at all. Screens were, of course, placed at suitable points to minimise these corrections. The ends of the mercury threads at A (of fig. 1) were read, also the positions of the mercury and oil in the gauges, and the corresponding influence on  $\delta v$  allowed for.  $\delta v$  amounts to about 0.5 gramme, this being almost entirely due to the difference in volume of the junctions at N and P (of fig. 2). As these parts are at a considerable distance from T, the correction involved has little uncertainty attached to it.

This list of corrections is formidable only in appearance. The corrections are very small. Tables are easily calculated, and the working out of a result involves only a few minutes' work.

#### *Sensitiveness of the Oil-gauge.*

With the apparatus as used the following table gives the approximate values of the sensitiveness of the gauge :—

- At  $0^{\circ}$  C. a change of pressure of 0.001 cm. of oil corresponds to a change of temperature of  $0^{\circ}00032$ .
- „  $100^{\circ}$  C. a change of pressure of 0.001 cm. of oil corresponds to a change of temperature of  $0^{\circ}00060$ .
- „  $445^{\circ}$  C. a change of pressure of 0.001 cm. of oil corresponds to a change of temperature of  $0^{\circ}00220$ .
- „  $1000^{\circ}$  C. a change of pressure of 0.001 cm. of oil corresponds to a change of temperature of  $0^{\circ}0070$ .

In other words, the sensitiveness diminishes with increase of temperature. This, however, is of no practical importance. The accuracy with which a temperature can be measured cannot be greater than the accuracy with which the fundamental interval has been determined. Thus, at  $1000^{\circ}$  C. the sensitiveness need only be 1/10 of that at  $100^{\circ}$  C., and this is nearly fulfilled, as the above table shows. When, in addition, one takes into account the difficulty of maintaining these high temperatures constant, it would appear that the sensitiveness is all that is necessary.

As regards the uniformity of the results, I think separate measurements of the coefficient of expansion should not differ from the mean by more than some 20 units, if the coefficient is expressed by six significant figures. This point will be again referred to when discussing the second series of experiments.

#### *Pressure Coefficient of the Bulbs.*

These are required, but only roughly, for some of the measurements. Thus, in finding the volume of the bulb T by filling it with mercury, the pressure of the latter produces an appreciable expansion of the bulb. This, of course, has to be allowed for. Again, in calibrating the apparatus (*i.e.* in finding the volume of the capillary tubes) it was necessary to have occasionally the bulbs full of mercury. It was therefore essential to allow for the changes of pressure produced by running out the liquid. Finally, in the ordinary use of the thermometer, a small correction is required, as has already been explained.

The pressure coefficient was determined by filling the bulb in question with mercury, and increasing or diminishing the internal pressure. The compressibility of the mercury has, of course, to be allowed for. The constancy of the coefficient obtained with both small and large changes of pressure affords a very good test of the presence or absence of small air bubbles.

The pressure coefficient for the two bulbs E was determined at  $0^{\circ}$  C.,

while for the bulb T it was determined at  $0^{\circ}$ ,  $100^{\circ}$ , and  $184^{\circ}$  with the following results:—

An external pressure of 1 cm. produces at—

$0^{\circ}$ C.	a change of volume of	0.00095	gramme.
$100^{\circ}$ C.	"	"	0.00099 "
$184^{\circ}$ C.	"	"	0.00106 "

#### *Volume of the Bulb.*

Before any experiments were made the bulb T was heated for many hours in sulphur vapour to anneal it. This produces an unknown change of volume. In general, therefore, the volume was determined at the end of each series by filling with mercury at  $0^{\circ}$  C. Each determination of the S.B.P. involves, however, a small change of the volume. It was noticed, in fact, that more mercury is run out of the bulb E in heating up T from the W.F.P. than has to be reintroduced in cooling down. This difference has been taken as a measure of the change of volume. The justification for this lies in the fact that it leads to *nearly* consistent values for the coefficient of expansion, although a total change of volume amounting to nearly 1 in 1000 has to be allowed for in the second series.

There is, however, another method by which the volume of the bulb T can be measured. Suppose all the bulbs are in ice, while both bulbs E are full of mercury. Now run out from the bulb E on the C side a weight of mercury somewhat greater than the approximately known capacity of the bulb T, allowing dry air to take its place. From the bulb E on the T side run out the estimated difference of these two volumes, allowing air to take its place, the pressures on the two sides being equal. This can be tested with the oil-gauge. The C side now contains a known quantity of air. Now turning off the stopcocks to prevent the entry of any further quantity of air, run out from the bulb E mercury so as to diminish the pressure on both sides. From a knowledge of the weights of this mercury, and the observation on the oil-gauge of any residual difference of pressure, it is evident that by an application of Boyle's law a value can be obtained for the volume of T. Any deviation of the gas from Boyle's law is, to all intents and purposes, compensated for. It must be remarked, however, that for a good determination by this method a much more accurate knowledge of the volume and temperature of the capillary tubes must be obtained than is required in the ordinary use of the thermometer. It is, perhaps, due to this that the results to be given immediately are not more closely concordant; unfortunately, owing to an accident to the bulb at the end of the experiment, the volume could not be checked by the weight method.

The following are the results obtained:—

First Measurement, filling with mercury—

January 11, 1900	.....	1276·015	} Mean, 1276·017.
„ 11 „	.....	1276·016	
„ 26 „	.....	1276·020	

Second Measurement, filling with mercury (after a further heating in sulphur vapour)—

March 19, 1900	.....	1274·828	} Mean, 1274·824.
„ 24 „	.....	1274·831	
„ 30 „	.....	1274·813	

Third Measurement, filling with mercury—

July 13, 1901	.....	1273·912.
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The substantial accuracy of this was confirmed a few days later by a rough measurement, which gave 1273·90 (not carried out in ice).

After this the bulb was heated for some 15 hours to a temperature of 600° to 700° C.

Fourth Measurement, Boyle's law experiment—

June 24, 1903	.....	1260·882	} Mean, 1260·980.
„ 25 „	.....	1260·831	
„ 25 „	.....	1261·054	
„ 25 „	.....	1261·035	
„ 26 „	.....	1261·099	

It is possible that the above table represents the concordance that one is able to get. On the other hand, there seems to be a sudden change after the second measurement, and in this connection it should be noted that an error in a weighing would entail an error in all the subsequent estimations of the volume of the bulb. It would have been better to have used throughout for each side a single vessel containing mercury from which to run back into E, or *vice versa*; this would limit the error caused by an erroneous weighing to the one experiment, but a loss of mercury by careless manipulation, if of unknown weight, would still affect all the subsequent determinations of the volume of the bulb. As regards the uncertainty introduced by an error in the volume of the bulb, calculation shows that a positive error of 1 in 10,000 in  $W_0$  produces a negative error of 50 units in the coefficient of expansion (with six significant figures) and a negative error of 0°·055 in S.B.P.

Fifth Measurement, filling with mercury (fresh bulb)—

July 11, 1906	.....	1265·391.
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*Coefficient of Expansion of Bulb.*

The important question of the expansion of the bulb made of Jena glass, 16 III, must now be dealt with, and it will be found necessary to discuss the results in some detail. The expansion of unit volume for any temperature  $t$ , measured on the constant-pressure scale, will be expressed in the form

$$[a + b(t - 100)]t.$$

The measurements were carried out by filling the bulb and the capillary tubes that lead to it with mercury and heating the bulb. The corresponding tubes on the C side were also filled, so as to compensate for the exposed stem of the thermometer. The calculations have been made, using the two available values for the absolute coefficient of expansion of mercury, viz., that due to Regnault as recalculated by Broch,\* and that due to Chappuis.†

*First Series of Experiments.*—After the observation in ice, the bulb T was heated up to W.B.P. in a double-jacketed apparatus of the ordinary form. After a small correction due to imperfect compensation of the capillary tubes, we get for the quantity of mercury driven out the following values:—

Date.	Temperature.	Observed weight.	Calculated weight.
1900.			
January 8 .....	100·165	19·857	19·856
" 8 .....	100·165	19·858	19·856
" 8 .....	100·168	19·858	19·856
" 25 .....	100·331	19·883	19·888

The two first values, marked for the same temperature, represent the mercury removed on heating up to W.B.P., and introduced on cooling down again to W.F.P. This was frequently done, and will not be again referred to. The last column is calculated by taking

$a = 23974 \times 10^{-9}$ , from Regnault's value for the expansion of mercury,  
or  $a = 24361 \times 10^{-9}$  „ Chappuis' „ „ „

A set of values was also taken at intermediate temperatures, the bulb T being heated in a large water bath kept vigorously stirred. At the higher

\* 'T. et M.,' vol. 2 (1883).

† 'T. et M.,' vol. 13 (1907). A small slip has occurred here in calculating the cubical from the linear coefficient of expansion of glass, so that the term in  $t^2$  for mercury should be 0·000 000 002 847, instead of 0·000 000 002 951. It is this corrected value that has been used.

temperatures the water was covered with a layer of oil to prevent cooling by evaporation. When the desired temperature was nearly reached, the flame was turned a little lower, so as to get a very flat maximum temperature, time readings being alternately taken of the weight and of a platinum thermometer. The indications of the latter were converted to the constant-pressure scale by assuming 444.53 as the S.B.P. at normal pressure. This perhaps, is slightly inconsistent, as the results of this paper lead to a lower value. It was, however, deemed inadvisable to make a change at this point. Now the expansion of mercury is given on the constant-volume scale. It becomes, therefore, necessary to allow for this small difference between the two scales. This has been done in accordance with D. Berthelot's\* formula.

Correcting as before for a small want of compensation in the exposed stem, we get the following table:—

Date.	Temperature on the—				Weight of mercury.
	Platinum scale.	Constant-pressure scale.	Constant-volume scale.	Normal scale.	
1900.					
January 20 .....	19·717	19·478	19·470	19·465	3·981
„ 9 .....	20·618	20·366	20·358	20·353	4·180
„ 10 .....	26·944	26·647	26·637	26·632	5·372
„ 22 .....	31·001	30·678	30·669	30·663	6·169
„ 9 .....	40·404	40·040	40·029	40·022	8·053
„ 10 .....	45·353	44·979	44·968	44·961	9·021
„ 22 .....	47·943	47·566	47·555	47·548	9·531
„ 24 .....	73·896	73·605	73·597	73·598	14·667

In calculating the mean value of  $b$  from the above data, I have omitted the second and fifth values, which give abnormally high values of  $b$ . These two weights (the two experiments were carried out on the same day) are not independent of one another, as the second weight was obtained by adding to the first the mercury driven out in heating up from  $20^{\circ}$  to  $40^{\circ}$ . It is hence thought probable that some error has crept into the first value. It will, in fact, be seen from the next table that a diminution of both weights by, say, 20 milligrammes would bring both into line.

The above experiments lead to the following value for  $b$ :—

$$b = 10.55 \times 10^{-9} \text{ (Regnault's mercury formula),}$$

$$b = 19.70 \times 10^{-9} \text{ (Chappuis' " " )}.$$

\* 'T. et M.,' vol. 13 (1907).

The second and fifth columns of the following table have been calculated, using the following formulæ for the expansion :—

$$\{23974 + 10.55(t-100)\} \times 10^{-9}, \quad (i)$$

$$\{24361 + 19.70(t-100)\} \times 10^{-9}. \quad (ii)$$

Weight of Mercury driven out.

Observed.	Calculated—				
	Regnault.		Chappuis.		
	Formula (i).	Formula (iii).	Formula (ii).	Formula (iv).	Formula (v).
3.931	3.928	3.918	3.932	3.943	3.916
4.130	4.106	4.096	4.110	4.121	4.093
5.372	5.365	5.353	5.369	5.382	5.349
6.169	6.171	6.158	6.175	6.190	6.153
8.053	8.038	8.023	8.039	8.056	8.015
9.021	9.019	9.005	9.020	9.038	8.996
9.531	9.533	9.519	9.533	9.551	9.508
14.667	14.669	14.667	14.665	14.684	14.651

The third, fifth, and sixth columns will be explained later.

#### *Second Series of Experiments.*

After this, the bulb was heated up for a long time in sulphur vapour. The volume diminished, as already explained, and later the following experiments were carried out :—

Date.	Temperature.	Observed weight.	Calculated weight.
1900.			
March 19	99.399	19.702	19.702
" 19	99.399	19.702	19.702
" 20	99.738	19.766	19.768
" 30	100.115	19.841	19.841

The last column is calculated by assuming for the expansion of the bulb—

$$a = 23868 \times 10^{-9} \text{ (from Regnault's mercury),}$$

$$a = 24254 \times 10^{-9} \text{ ( " Chappuis' " )}.$$

It will be noticed that heating has diminished the value of  $a$ . This has been noticed by other observers.



To obtain a better value for  $b$ , it was determined to heat the bulb to a higher temperature, and the vapour of boiling aniline seemed the most convenient for the purpose. The aniline was boiled in a beaker about 40 cm. high and 9 cm. diameter. The bulb, with the platinum thermometer in contact with it, was surrounded by a copper cylinder to stop radiation and prevent cooling by convection currents. This was also aided by placing two horizontal tin-plates, one immediately over the copper cylinder and the other a few centimetres above this. These plates were of nearly the same diameter as the beaker, and had five holes punched in them to allow the various tubes and platinum thermometer to pass through. A small asbestos umbrella was placed on the stem of the weight and of the platinum thermometer to prevent the condensed aniline trickling down the bulb. In addition, two or three layers of asbestos paper were wrapped round the beaker. Three experiments were carried out, between each of which the bulb was emptied and refilled :—

Date.	Temperature on the—				Weight of mercury.
	Platinum scale.	Constant-pressure scale.	Constant-volume scale.	Normal scale.	
1900.					
March 28 .....	181·227	183·450	183·490	183·522	35·935
„ 23 .....	181·563	183·798	183·838	183·870	36·003
„ 23 .....	181·563	183·798	183·838	183·870	36·015
„ 29 .....	181·661	183·901	183·941	183·973	36·022
„ 29 .....	181·661	183·901	183·941	183·973	36·022

The mean values of  $b$  calculated from these experiments are :

$$b = 4.20 \times 10^{-9} \text{ (from Regnault's formula),}$$

$$b = 23.47 \times 10^{-9} \text{ ( „ Chappuis' „ ).}$$

We hence have the two following formulæ :

$$\{23868 + 4.20(t-100)\} \times 10^{-9}, \quad (\text{iii})$$

$$\{24254 + 23.47(t-100)\} \times 10^{-9}, \quad (\text{iv})$$

while, to show the change introduced by a variation of  $b$ , the following formula has also been used :

$$\{24254 + 10(t-100)\} \times 19^{-9}. \quad (\text{v})$$

Columns corresponding to these formulæ have already been given in connection with the experiments between  $0^\circ$  and  $100^\circ$ . The following table gives the corresponding calculations for the aniline values :

## Weight of Mercury driven out.

Observed.	Calculated.				
	Regnault.		Chappuis.		
	Formula (i).	Formula (iii).	Formula (ii).	Formula (iv).	Formula (v).
35·935	35·789	35·938	35·986	35·938	36·201
36·003	35·856	36·004	36·054	36·005	36·269
36·015	35·856	36·004	36·054	36·005	36·269
36·022	35·874	36·024	36·074	36·025	36·290
36·022	35·874	36·024	36·074	36·025	36·290

It will be noticed that Regnault's value for mercury makes  $b$  diminish with rise of temperature, while Chappuis' shows an increase. It is true that Chappuis carried out experiments only between  $0^{\circ}$  and  $100^{\circ}$  C. As, however, his formula contains the same number of terms as Regnault's, it seems reasonable to extrapolate it. We have evidence from other observers that  $b$  diminishes with temperature. Kamerlingh Onnes,\* from experiments on the same kind of glass between  $-182^{\circ}$  and  $100^{\circ}$ , is quite sure of the fact. Experiments at the Reichsanstalt† between  $-190^{\circ}$  and  $500^{\circ}$  indicate this as a general law for all substances tried, such as glass, porcelain, metals, and alloys, the only exception being brass. No experiments, however, are given for this particular kind of glass between these temperatures.

Chappuis' values for mercury were obtained by a weight thermometer method in a tube of *verre dur*, the linear expansion of which was measured directly between two marks made on the tube itself. These marks were not, unfortunately, on the neutral fibres. But apart from this, when one takes into consideration the method by which the ends of a tube are sealed off so as to form a bulb, and the change in the coefficient of expansion that must result from this, it seems unjustifiable to calculate the cubical from the linear coefficient, unless the tube has been very thoroughly annealed. This does not appear to have been done; at all events, no mention is made of it. The value of the mean cubical coefficient of expansion obtained was

$$(21696 + 16\cdot49t) \times 10^{-9}.$$

This is in good agreement with a value obtained by Harker and Chappuis,‡

$$(21801 + 15\cdot536t) \times 10^{-9},$$

\* 'Comm. Phys. Lab. Leiden,' No. 95b.

† 'Ann. der. Phys.,' 4. F., vol. 6 (1901), p. 36, and vol. 22 (1907), p. 631.

‡ 'Phil. Trans.,' A, vol. 194 (1900), p. 74.

which is, presumably, an independent measurement. On the other hand, the second term does not agree with a value obtained for the same kind of glass at the Reichsanstalt: \*

$$(22252 + 10.83t) \times 10^{-9}.$$

Experiments between  $0^{\circ}$  and  $100^{\circ}$  on Jena glass, 16 III, carried out at the Reichsanstalt, give for the mean coefficient,

$$\{24238 + 10.71(t - 100)\} \times 10^{-9}.$$

[ $t$  is here on the normal scale, but for this purpose the difference can be neglected.] The expansion was observed on the neutral fibres, but the glass had not been annealed, except that it was slightly softened with a Bunsen burner to straighten it. It will be noticed that the " $b$ " term is in excellent agreement with the value (10.55) deduced from my experiments with Regnault's values. This agreement has led me to prefer the latter observer's values for mercury, especially as use has to be made of the  $184^{\circ}$  value; a fair conclusion seems to be that the question of the true coefficient of expansion of mercury must still be regarded as an open one. In calculating, therefore, the S.B.P., the following formula has been used:—

$$\{23868 + 4.20(t - 100)\} \times 10^{-9},$$

where  $t$  is expressed on the constant-pressure scale; but it is useless to disguise the fact that it leaves the true value of the S.B.P. still uncertain. To change  $b$  from, say, 5 to 20 will raise the temperature by about  $1^{\circ}.41$ , and to change  $a$  from 23,868 to 24,254 will raise the temperature by a further  $0^{\circ}.06$ .

#### *Recovery of Zero.*

It was interesting to see if any recovery of zero could be observed after the aniline points. Two sets of observations were taken; readings at the W.F.P. could only be taken about three quarters of an hour after the aniline point. Readings of the mercury on both sides are observed, and it is to the difference of the readings that attention must be paid, so as to eliminate emergent stem errors.

\* 'Wiss. Abh. Reichs.,' vol. 2, p. 129.

March 27, 1900.—Put out flame (heating the aniline) at 12.15 P.M., cooled bulb rapidly, first with hot, then cold, water. Started piling the ice at 12.40 P.M.

12.55 P.M. readings .....	{ T side .....	9.15
	{ C „ .....	9.43
1.15 „ „ .....	{ T „ .....	9.14
	{ C „ .....	9.42
2.30 „ „ .....	{ T „ .....	9.12
	{ C „ .....	9.41
4.45 „ „ .....	{ T „ .....	9.12
	{ C „ .....	9.40

The second set is as follows :—

March 29, 1900.—Put out flame at 3.40 P.M. Began adding ice at 4.10 P.M.

4.30 P.M. readings .....	{ T side .....	10.05
	{ C „ .....	10.06
4.50 „ „ .....	{ T „ .....	10.05
	{ C „ .....	10.06

March 30, 1900.—

11.50 A.M. „ .....	{ T „ .....	10.06
	{ C „ .....	10.06

In the latter case in the course of 20 hours a contraction of the bulb equivalent to  $0^{\circ}005$  was observed. As, however, readings were only taken to  $0.01$ , it is possible that even this is mere error of observation.

When dealing with the determination of the S.B.P., some evidence will be given indicating an appreciable change in the course of a day.

#### *The Resistance Measurements.*

As the S.B.P. was observed directly on the air thermometer, and not through the intermediary of the platinum thermometer, the latter was only used in obtaining the expansion of the glass, where the accuracy of the readings is of less importance. It, therefore, seems unnecessary to enter into any long description here. It may briefly be stated that the box used was one made by the Cambridge Instrument Co., and is similar to one already described by Dr. Chree.\* The coils were all replaced by silver-soldered manganin coils annealed for about 10 hours at  $140^{\circ}$  C. Three extra coils were added, as the thermometer used had a resistance at  $0^{\circ}$  C. of about 10 ohms. The calibrated bridge wire was shunted, so that 40 cm.

\* 'Roy. Soc. Proc.,' vol. 67, p. 6.

were equivalent to 0.1 ohm. The resistances were occasionally tested against each other. In making the measurements the galvanometer circuit is kept closed, while the slider is shifted, until no deflection is observed on reversing the key in the battery circuit. Such a point could always be obtained. To eliminate heating effects, this balancing point was obtained first with one cell, then with two in series. The heating effect in the second case was assumed to be four times that in the first. As the latter never amounted to more than  $0^{\circ}025$ , and later with a more sensitive galvanometer was much less, there is little uncertainty in the correction for the purpose required. Leakage in the thermometer was frequently tested for.

#### *The Barometers.*

It is, of course, necessary to read the barometer for calculating the W.B.P. and the S.B.P. Originally, a Hick's barometer constructed on Fortin's principle was used. This bears a Kew certificate, dated December, 1873, giving the correction as  $+0.005$ . The vernier reads to 0.01, but was estimated to 0.003. Later, a barometer was constructed, the design of which is due to Professor Callendar. The object is to get the whole barometer immersed in water, so as to ensure a true temperature correction. Fig. 3 will make clear its construction.

A and B are two platinum-iridium needles, about 7.8 cm. long, fused in the glass. Their difference of length was determined after fusion, but before this part was joined on to the barometer, so that it was not necessary to make the observations through the glass. The distance apart is about 76 cm. C is a small air-trap; D serves for evacuation, and is afterwards fused off. The tube E communicates by rubber and glass tubes with a vessel F containing mercury, and a graduated oil manometer G open to the atmosphere at H. The barometer and rubber tube are surrounded by a wide tube full of water, the temperature being read on two thermometers. F is surrounded by cotton-wool to prevent any rapid change of temperature; an obvious arrangement permits the pressure in F to be varied. The quantity of mercury in AB is adjusted, so that when one surface touches the lower point of A the other should be practically touching B. The process of reading the barometer consists, then, in bringing the surface of the mercury first into contact with A, then with B, and reading the manometer on each occasion. If, for this *small* adjustment, we can assume the tube at A to have the same diameter as the tube at B, the arithmetic mean of the two manometer readings will give accurately the difference between the barometric pressure and that due to a column of mercury equal in height to the distance between the lower points

of the needles. An electrical arrangement for the contact was first tried, but very soon the contact at B became very bad, and an optical adjustment was adopted in its place. This barometer was found to work very well, but in the course of a few years the mercury and glass at B became dirty, partly no doubt due to water vapour passing through the rubber tube.\*

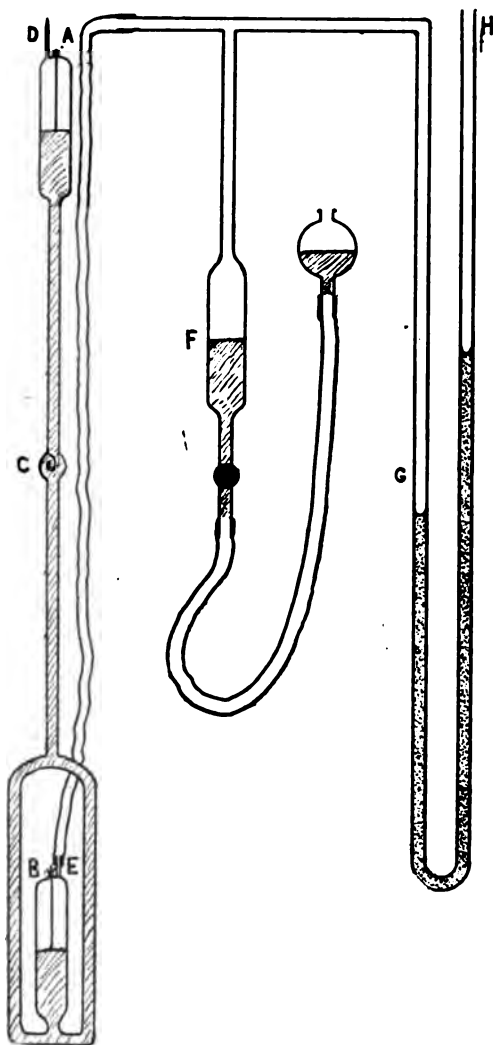


FIG. 3.

As the needles at A and B project above the tube, it is possible at any moment to verify the distance between them. This was done several times

\* Compare Rayleigh, 'Coll. Pap.,' vol. 4, p. 42.

with a cathetometer, the scale of which was compared with an invar scale procured later:—

Length at 11° C.

April, 1901 .....	76·348
October, 1901 .....	76·345
December, 1901.....	76·344

After the invar scale was procured, the length was compared directly with this:—

May, 1902 .....	76·3462
December, 1906 .....	76·3445

The invar scale was standardised once at Sèvres, and once at Teddington a few years later.

To obtain the coefficient of linear expansion, advantage was taken of a change of temperature in May, 1902:—

May 7, 8, and 9, 1902 .....	76·3462 at 11° C.
May 27 and 28, 1902 .....	76·3524 at 19°·3 C.

This is the length between the upper points, which were adjusted so as to be vertically one over the other. To obtain the distance between the lower points, three small corrections must be applied, one for the difference in length between the two needles, and the other two for the want of verticality of each needle.

The Hicks barometer was compared with this later one, and the correction for the former found to be +0·007. As the vernier only reads to 0·01, the agreement with the value given by the Kew certificate (+0·005) was considered satisfactory.

A small correction, due to a difference in height between the reservoir of the barometer and the bulb of the air thermometer, was applied to the barometer readings. Further, in calculating the pressure due to a given column of mercury,  $g$  in the laboratory was taken as equal to 1·00058  $g_{45,0}$ .

In addition to the above barometer, a compensated barometer was used, the construction of which will be seen from fig. 4 (Callendar's Patent, No. 10,456, 1891).

The tube AB contains dry air up to a level E. The annular space between AB and CD, and the tubes to the levels E and F, contain Fleuss pump oil. The tube F is open to the atmosphere. The tubes G and H, which are finally sealed off, are convenient for filling the apparatus. The assumption is made that the air in AB is at the same temperature as the oil in CD. Knowing the coefficient of expansion of the oil, the volumes of AB, CD and the tubes are calculated, so that a change of temperature only of the atmosphere should make no difference in the level of the oil in E, while a change of pressure as

measured on a mercury barometer should be magnified 10 times on the tube E, which is accordingly graduated to read changes of pressure. If the volumes of the bulbs are not quite in the right ratio, small pieces of glass rod

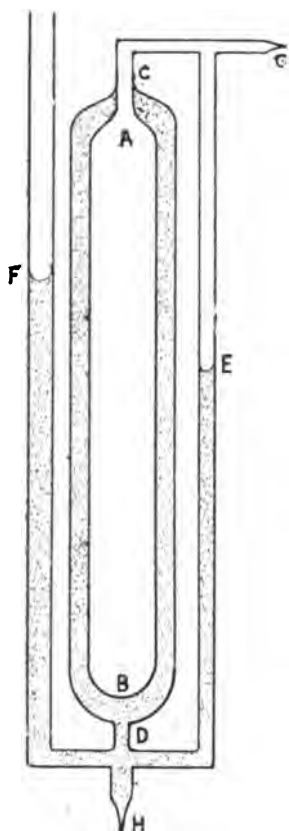


FIG. 4.

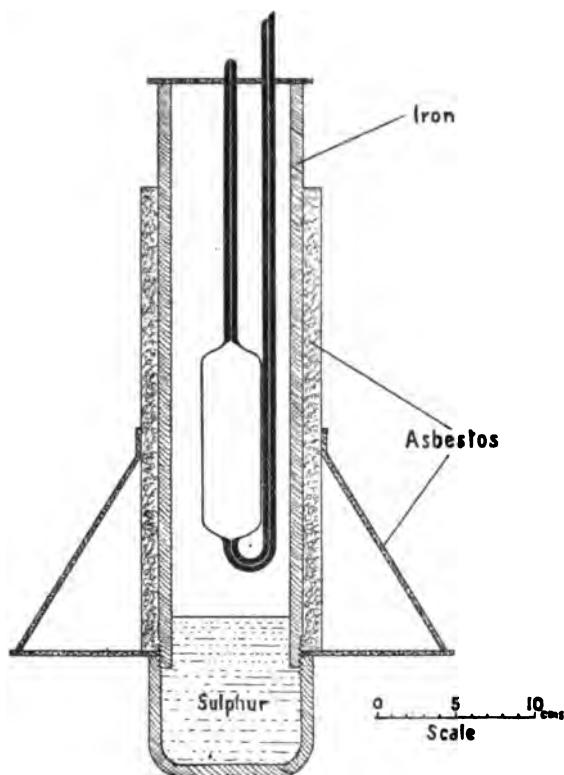


FIG. 5.

can be introduced through G or H to correct this. In practice, the standard barometer was read once during the day, and the changes of pressure in the course of a day read on the compensated barometer. A considerable saving in time was thus effected.

#### *Course of the Experiments.*

Only three temperatures were observed on the thermometer, viz., W.F.P., W.B.P., and S.B.P. For the W.F.P. the ice was obtained in  $\frac{1}{2}$ -cwt. blocks, washed with distilled water, and crushed very fine. The interstices were filled up with distilled water, or water from melted ice. Although the purity was occasionally tested with silver nitrate, this was, unfortunately, not done as a matter of routine. The W.B.P. apparatus was of the ordinary double-jacketed form. The lid of this was perforated for the various tubes, and leakage of steam



prevented by plugging with asbestos made into a pulp by moistening with a little water. No manometer was attached to this, as a similar hypsometer, but taller, and of smaller cross-sectional area, showed a practically negligible difference of pressure. The values of the W.B.P. are taken from Harker and Chappuis' paper.

The S.B.P. apparatus is shown in fig. 5 with the air thermometer in position (the tubes on the C side are omitted). The latter was sometimes accompanied by a platinum thermometer. To prevent radiation, the bulb was surrounded by a tinplate screen of the usual type (not shown), while above this two horizontal plates were placed (also not shown), almost closing the cross-section. These plates were, however, a source of much trouble. It was practically impossible to put them in place without scraping the sides of the glass tubes. This, after a time, always resulted in scratching, and later cracking, the tubes, and so putting an end to the experiments. Dr. Harker informs me that the prolonged action of sulphur vapour on the French *verre dur* is to make it very brittle. This can easily be shown not to be a mere temperature effect. The accidents may, of course, have been due to this.

In reducing the S.B.P. to normal pressure, the correction has been taken equal to 0.88*h*; no correction has been made for the pressure due to the sulphur vapour.

Some experiments were made to test the agreement of the S.B.P. obtained in a large and small iron boiler of the same type. The same platinum thermometer was immersed to the same height in both:—

Small Boiler. Diameter, 3.7.

July 16, 1903—

No vertical screen, two horizontal discs..... pt. = 419.691 at 75.176  
= 420.328 „ 76

July 17, 1903—

A vertical screen „ „ ..... pt. = 419.923 „ 74.960  
= 420.726 „ 76

Larger Boiler. Diameter, 7.6.

July 17, 1903—

No vertical screen, two horizontal discs..... pt. = 419.548 „ 74.960  
= 420.351 „ 76

July 20, 1903—

A vertical screen „ „ ..... pt. = 420.861 „ 76.125  
= 420.764 „ 76

July 20, 1903—

Two vertical screens „ „ ..... pt. = 420.916 „ 76.189  
= 420.770 „ 76

*The Experiments.*

The bulbs and tubes were cleaned first with hot nitric acid, then hot potassium hydrate, then again nitric acid, and finally the whole apparatus was several times completely filled with distilled water. In the final drying, the bulbs C and E were at  $100^{\circ}\text{C}$ ., while T was in sulphur vapour, and the whole apparatus repeatedly evacuated with a Fleuss pump. The thermometer was allowed to cool full of air at atmospheric pressure, and when cool it was finally evacuated and filled with air at  $0^{\circ}\text{C}$ . The air was purified by passing through a tube containing potassium hydrate, then sulphuric acid, and finally phosphorus pentoxide.

## First Set.

March 9, 1900 .....	W.F.P.	} 0·003 671 25 0·003 671 18 0·003 671 53	
	W.B.P.		
	W.F.P.		
	W.B.P.		
March 13, 1900 .....	W.F.P.	} 0·003 671 63	
	W.B.P.		
March 14, 1900 .....	S.B.P.	} 443·47* at 76.	
	Diminution in volume of bulb = 0·610 gr.		
March 15, 1900 .....	W.F.P.		
	W.B.P.	} 0·003 671 15	
March 16, 1900 .....	S.B.P.		
	Diminution in volume = 0·246.	} 442·481 at 74·865 = 443·480 at 76.	
March 17, 1900 .....	W.B.P.		
	W.F.P.		
	Mean coefficient .....	0·003 671 31	
	Final volume of bulb .....	1274·824	
	Pressure .....	76·7	

\* In this my first experiment with the large sulphur boiler, the evolution of vapour was so great that I turned the flame low—too low, in fact. The above temperature is obtained through the intermediary of the platinum thermometer which was alongside. The highest actual temperature measured was 443·495. The barometer on that day was 77·4.

## Second Set.

June 25, 1901 .....	W.F.P.	} 0·003 669 86	
	W.B.P.		
June 26, 1901 .....	W.B.P.	} 0·003 670 42	
	W.F.P.		
June 27, 1901 .....	W.B.P.	} 0·003 670 33	
	W.F.P.		
June 28, 1901 .....	W.B.P.	} 0·003 669 85	
	W.F.P.		
	W.B.P.	} 0·003 669 64	
	W.F.P.		
	W.B.P.	} 0·003 669 74	
	W.F.P.		
	W.B.P.	} 0·003 669 57	
	W.F.P.		
	W.B.P.	} 0·003 669 63	
	W.F.P.		
July 1, 1901 .....	S.B.P.	}	
	Change of volume = 0·632		
July 2, 1901 .....	W.B.P.	} 0·003 670 37	} 442·834 at 75·289 = 443·504 at 76.
	W.F.P.		
July 3, 1901 .....	S.B.P.	}	
	Change of volume = 0·226		
	W.F.P.	}	} 443·134 at 75·472 = 443·599 at 76.
	W.F.P.		
July 4, 1901 .....	S.B.P.	}	
	Change of volume = 0·148		
	W.B.P.	} 0·003 671 15	} 443·909 at 76·209 = 443·725 at 76.
July 5, 1901 .....	W.F.P.		
	W.B.P.	} 0·003 670 28	
	W.F.P.		
	W.B.P.	} 0·003 670 05	
	W.F.P.		
July 8, 1901 .....	S.B.P.	}	
	Change of volume = 0·181		
	W.F.P.	} 0·003 670 08	} 444·130 at 76·480 = 443·708 at 76.
July 9, 1901 .....	W.B.P.		
	W.F.P.	} 0·003 670 65	
	W.F.P.		
Mean coefficient .....		0·003 670 12	
Final volume of bulb .....		1273·912	
Pressure .....		75·3	

If the total changes of volume given above are added on to this final volume, it will make the initial volume greater than the final volume of the

first set. This, of course, is not impossible, as the bulb had a long time in which to recover. But the first set of coefficients is distinctly lower than the rest; it thus appears that the change of volume deduced is too large.

Now, as regards other variations observed in the coefficients. The second and third are both calculated from the same W.F.P. It is possible that the ice was not quite pure in this case, as the variation seems to exceed the experimental error.

On July 4, when a W.B.P. was taken immediately after a S.B.P., this coefficient comes out very large. The same effect will be noticed again in the fourth set. On July 8, a W.F.P. is taken just after a S.B.P., and the corresponding coefficient is smaller than the succeeding one, though the difference here is small. It is *as if* the bulb gets larger again; the effect may, of course, be due to something occurring in the gas. It should not be difficult to decide between the two explanations.

## Third Set.

June 26, 1903 ...	W.F.P.	} 0·003 671 55	
	W.B.P.		
June 29, 1903 ...	W.F.P.	} 0·003 671 26	
	W.B.P.		
July 1, 1903 .....	W.B.P.	} 0·003 670 91	
	S.B.P.		
	Change of volume = 0·147	} 444·201 at 76·611 = 443·842 at 76.	
July 2, 1903.....	W.F.P.		
July 3, 1903.....	W.B.P.	} 0·003 671 22	
	S.B.P.		
		} 443·920* at 76·170 = 443·770 at 76.	
Mean coefficient .....	0·003 671 23		
Initial volume of bulb .....	1260·980		
Pressure .....	76·0		

In this case the volume was determined by the use of Boyle's law; it has not, therefore, the same claim to accuracy as in the other cases.

\* This is deduced from the preceding W.F.P., the experiments having come to a conclusion at this point, owing to an accident.

## Fourth Set.

June 21, 1906 .....	S.B.P.	} 444·179 at 76·739 = 443·529 at 76.
	Change of volume = 0·174	
June 22, 1906 .....	W.B.P.	
	W.F.P.	} 0·003 671 06
June 27, 1906 .....	S.B.P.	
	Change of volume = 0·012	
	W.B.P.	} 443·472 at 75·843 = 443·610 at 76.
June 28, 1906 .....	W.F.P.	
	W.B.P.	
	W.F.P.	} 0·003 670 18
	W.B.P.	
	S.B.P.	
	Change of volume = 0·030	} 443·140 at 75·490 = 443·589 at 76.
June 29, 1906 .....	W.F.P.	
	Mean coefficient .....	0·003 670 62
	Final volume .....	1265·391
	Pressure .....	76·2

The mean coefficient is that derived from the first and last; the second has been omitted for reasons that have already been referred to. If the mean of the three had been taken, the S.B.P. would be lower by 0°·06. On June 27, after the W.B.P., an attempt had been made to obtain a W.F.P. Owing to want of time, it was considered unsatisfactory and cancelled the same evening. If any reliance can be placed on the observation, there was a diminution of pressure by the next day of 0·002 cm. mercury, and the W.B.P. was taken before this; it is obvious, then, what a serious error must arise owing to the uncertainty as to the behaviour of the glass.

Eleven values of the S.B.P. have thus been obtained, the lowest of which is

443·47,

and the highest 443·84.

The mean is 443·62;

while, if we miss out the third set as being less reliable, the mean is

443·58.

In conclusion, I must express my indebtedness to Professor Callendar for constant help during the progress of the experiments; I have also to thank Dr. C. E. Guillaume for advice in procuring and standardising the invar scale.

*Note on the Boiling-point of Sulphur.*

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As I have been partly to blame for the delay in the publication of the observations described in the preceding paper by Mr. N. Eumorfopoulos, it seems right that I should make a brief statement, by way of apology, with regard to the object of the work and the causes which have led to the delay.

The determination of the boiling-point of sulphur by Mr. E. H. Griffiths and myself in 1890\* was made with the same air thermometer as that employed in my original experiments of 1887,† and gave the same value for the difference-coefficient of the platinum thermometer. The result depended, however, on the scale of the constant-pressure air thermometer, and the correction for the expansion of the bulb was deduced from observations of the linear expansion over the range 0° to 500° C. of a piece of glass tube from which the bulb was made. Some uncertainty was introduced also by changes in the volume of the bulb at a temperature of 450° C.

Shortly afterwards I succeeded in devising a much more delicate type of gas thermometer,‡ with compensated connecting tubes, and independent of barometric measurements, the bulb of which could be used as a mercury weight thermometer in determining the expansion correction. In the hope of obtaining a more accurate verification of the boiling-point of sulphur, as well as of the difference-formula for the platinum scale between 0° and 450° C., I undertook a series of observations in 1893 in conjunction with Mr. E. H. Griffiths and Mr. G. M. Clarke, employing two gas thermometers precisely similar to that described by Mr. Eumorfopoulos, except that they were made of English lead glass. One of these thermometers was filled with air and the other with hydrogen in the first instance. At a later stage both were filled with nitrogen, because it was found that hydrogen reduced the lead glass at high temperatures, and there was some reason to suspect action of oxygen on the mercury.

The English lead glass, when it had once been annealed in sulphur vapour, proved remarkably free from changes of volume, and there was no difficulty in determining its expansion in terms of mercury between 0° and 100° C., with

\* 'Phil. Trans.,' A, 1891.

† 'Phil. Trans.,' A, 1887.

‡ 'Roy. Soc. Proc.,' vol. 50, p. 247.

an accuracy of the order of 1 or 2 milligrammes of mercury in 1300 grammes, corresponding to an error of about  $1/2000$  degree of temperature, but it was found that the results could not be brought into satisfactory agreement with Regnault's formula, or with the previous determination by the linear expansion method. Assuming Regnault's formula for the absolute expansion of mercury,

$$V/V_0 = 1 + 0.00017901t + 0.000,000,0252t^2,$$

the expansion of the lead glass bulbs could be approximately represented by the formula

$$V/V_0 = 1 + 0.00002242t + 0.000,000,0240t^2,$$

which may also be written (adopting the form employed by Eumorfopoulos)

$$V/V_0 = 1 + \{0.00002482 + 0.000,000,0240(t-100)\}t.$$

The expansion did not appear to follow accurately a parabolic law, but if a parabolic formula were assumed for mercury, the  $b$  term, or the coefficient of  $t^2$ , came out nearly the same as for mercury. The observations could be almost equally well represented by assuming the expansion of both mercury and glass to be uniform between  $0^\circ$  and  $100^\circ$  C., an assumption which also appeared to represent Regnault's observations on mercury over this range within the limits of experimental error. The effect of the  $b$  term on the temperatures deduced by gas thermometer is about 130 times as great at  $445^\circ$  C. as at  $50^\circ$  C., amounting, if  $b = 24 \times 10^{-9}$ , to  $2^\circ.64$  at the S.B.P., and to  $0^\circ.020$  at  $50^\circ$  C. Since the expansion did not appear to follow accurately a parabolic formula, it seemed useless to attempt an extrapolation. It appeared probable that the  $b$  term for mercury was not constant, as in Regnault's formula, but increased with rise of temperature; and that it would be necessary to make a redetermination of the absolute expansion of mercury, and also to employ the weight thermometer method at much higher temperatures than  $100^\circ$  C., if any certain result were to be obtained by this method. I accordingly designed a multiple manometer for the absolute expansion of mercury, in which the expansion to be measured was increased to about eight times that obtained by Regnault; and I hoped, by employing platinum thermometers and other refinements not available in his time, to be able to secure a much higher order of accuracy in this fundamental determination. At this point the work was interrupted by my appointment as Professor of Physics at McGill College, Montreal, in October, 1893, and I was unable to resume it until my return to University College in 1898.

Meanwhile the Kew Committee and the International Bureau of Sèvres, recognising the importance of the work, had collaborated in arranging a redetermination of the boiling-point of sulphur and of the scale of the

platinum thermometer, which was undertaken by Messrs. Chappuis and Harker.\* The results of their work with a constant-volume nitrogen thermometer led to a somewhat higher value, namely  $445^{\circ}26$  C., of the S.B.P. than the value  $444^{\circ}53$  C. obtained with the constant-pressure air thermometer. The difference between these two values was too great to be explained by the difference between the scales of the constant-volume and constant-pressure thermometer, which probably amounts to only  $0^{\circ}3$  at this point.† But as I pointed out at the time,‡ the uncertainty of the expansion correction was sufficient to account for a much larger discrepancy. The results of Messrs. Chappuis and Harker depended on the extrapolation of a formula for the linear expansion obtained from observations over the range  $0^{\circ}$  to  $80^{\circ}$  C., which gave a comparatively high value for the coefficient  $b$ . They subsequently adopted a different formula for the expansion, which had the effect of reducing their result to  $444^{\circ}77$  C. on the constant-volume scale, which is in practically perfect agreement with  $444^{\circ}53$  on the constant-pressure scale.

Having regard to the excellence of this agreement it might have appeared superfluous to proceed further. But the uncertainty of inferring the cubical from the linear expansion still remained, and it was desirable to obtain a more accurate verification of the scale of the platinum thermometer at ordinary temperatures for the reduction of experiments on the variation of specific heat. My original gas thermometer had been broken on the way out to Canada, and again on the way back. I therefore had another constructed of Jena glass to fit the same stand, hoping that the new glass would prove less troublesome in respect of change of volume. At the same time I proceeded with the construction of the apparatus already designed for the absolute expansion of mercury. This was nearly finished, and several determinations of the S.B.P. had already been made by Mr. Eumorfopoulos, when I had to leave University College in April, 1902. After several fruitless efforts to find a place to set up the apparatus at the Royal College of Science, I had finally to await the completion of the new buildings, then in course of erection. I was able to proceed with the erection of the apparatus at the end of last year, and some preliminary experiments which promise well have already been made with it. The apparatus seems likely to realise the same order of accuracy in the absolute expansions of mercury as in the weight-thermometer tests of the bulb. It was designed with that intention, but, until it was set up and tested, it was difficult to foresee

\* 'Phil. Trans.,' A. vol. 94, p. 74.

† 'Callendar, 'Phil. Mag.,' 1903, p. 93.

‡ 'Phil. Mag.,' December, 1899, p. 544.



whether effects of lag and viscosity might not be serious in so great a length of tubing.

It will be seen from the experimental results given by Mr. Eumorfopoulos in the preceding paper that the hopes which I had formed of Jena glass were far from realised. The continual changes of volume of the bulb were among the chief difficulties encountered, and are doubtless indirectly responsible for the apparent variations in the coefficient of expansion observed, which considerably exceed the limit of accuracy of reading. An alternative method of treating the observations, which I adopted in the experiments of 1890, would be to calculate the changes of volume by assuming a constant value of the coefficient. This would tend to eliminate the accumulation of accidental errors in a long series of weighings. In spite of the changes of the bulb, and of other possible sources of error, it is obvious that the results obtained by Mr. Eumorfopoulos are entitled to great weight, and will lead to a more certain value of the S.B.P. when the expansion of mercury has been more accurately determined. Publication has been delayed from time to time in the hope that these difficulties might be surmounted, but as it now appears certain that glass is an unsuitable material for accurate work of this nature, it would be useless to delay any longer. The description of the method and apparatus employed, which has not been previously published, although the apparatus has been in existence for so many years, may prove serviceable to others engaged in similar work.

That the final result given, namely,  $443^{\circ}58$  C. for the S.B.P., should be nearly  $1^{\circ}$  lower than the value previously admitted may appear surprising. But it must not be forgotten that, if Chappuis' formula for the expansion of mercury had been adopted, the result would have been  $445^{\circ}8$  C. approximately, or more than a degree higher than the old value. This illustrates the necessity for a redetermination of the expansion of mercury. At the same time it must be admitted that Regnault's formula is more likely to be right at the higher temperatures, and that the old value of the S.B.P. is likely to be too high in consequence of the probable error involved in deducing the cubical coefficient from the linear expansion of a tube.

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*On Optical Dispersion Formulæ.*

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In the half century that elapsed from the time when Cauchy published his memoirs on dispersion, the only measurements of refractive indices that were available for the test of any theory were confined to the neighbourhood of the visible spectrum. They extended from somewhat beyond  $0.2\mu$  to about  $0.8\mu$ , *i.e.* over a range of two octaves. In this range the variation of refractive index for most substances is small, and it is not surprising that, by a proper adjustment of constants, a variety of different formulæ may be made to fit the experimental facts. More recently, however, the range of observations has been immensely extended, so that we now have a large number of determinations of refractive indices for various wave-lengths extending from less than  $0.2\mu$  to  $22.3\mu$ . With a knowledge extending over this range of about seven octaves, there is more hope of testing the merits of different dispersion formulæ. Accordingly, when, in 1879, Mouton made the first considerable extension in the direction of great wave-lengths, he found that, with the same number of constants, the formula of Briot represented the facts much better than did the older one of Cauchy, and the same result was reached by Langley in 1884 and 1886. The still more extended observations of Paschen, Rubens, E. F. Nichols, and A. Trowbridge, published at various dates from 1892 to 1897, have shown that Sellmeier's formula\*

$$n^2 = K + c_1/(\lambda^2 - \lambda_1^2) + \dots$$

is the only one of those that have been tried that is in thorough accord with the observed values of the refractive indices over the whole range of the experiments.

It must, however, be admitted that there are various doubts and difficulties connected with the development of this formula from a sound dynamical basis in any of the various forms of its presentation, whether we follow directly the arguments of Sellmeier, Ketteler, Helmholtz, or Kelvin, or express their ideas in the language of electron theory as Drude and others have done. But apart from difficulties as to the exact character of the reaction between ether and matter, and doubts as to the validity of certain

\* Usually quoted now as the "Ketteler-Helmholtz formula."

dynamical principles employed in its evolution, the Sellmeier formula is open to two serious objections.

(1) When the wave-length is indefinitely increased, the formula gives  $n^2 = K$ , so that, on the electromagnetic theory of light,  $K$  should be the dielectric constant of the medium. The values of  $K$ , determined by the Sellmeier formula from the observations of refractive indices by Rubens and Nichols, are 6.09, 4.58, 5.18, and 4.55 for fluorite, quartz, rocksalt, and sylvin respectively, and the slightly different observations of the other physicists mentioned above make scarcely any appreciable change in the estimate of  $K$ . Thus Langley finds  $K = 5.1747$  for rocksalt, while Rubens and Trowbridge find  $K = 5.179$ . Unfortunately there is not the same agreement amongst different direct determinations of the dielectric constant. For fluorite the constant is 6.8, 6.7, or 6.9, according to Curie, Romich and Nowak, or Starke; while for quartz these observers find 4.55, 4.6, and 4.73 respectively. For rocksalt Curie gets 5.85, Thwing 5.81, and Starke 6.29; and the last named observer gives 4.94 as the dielectric constant of sylvin. Taking the mean of these for the different substances, we find 6.8, 4.63, 5.98, and 4.94, as compared with 6.09, 4.58, 5.18, and 4.55 of the dispersion formula. It will be noted that the differences are in all cases in the same direction, and, except in the case of quartz, are considerable, being more than 10 per cent. of the quantity considered.

(2) A more serious discrepancy reveals itself on comparing the calculated values of  $\lambda_2$  and the observed positions of the absorption bands of different substances. According to the theory, the absorption band should be found very near to  $\lambda_2$ , although not absolutely coincident with it. The values of  $\lambda_2$ , calculated from the formula to fit in with the experimental determinations of refractive indices by Nichols, Rubens, and Paschen for rocksalt, sylvin, and fluorite are 56.12, 67.21, and 35.47 respectively, whereas the absorption bands were found at 51.2, 61.1, and 23.7. Here, again, the differences are in all cases in the same direction, and are of an order of magnitude altogether beyond the limits of experimental error. The difference is greatest for fluorite, where it amounts to nearly  $12\mu$ , but the smallest difference, about  $5\mu$  for rocksalt, is at least five times too great to be ascribed to errors in the experiments. It must be borne in mind that the formula involves not  $\lambda_2$  but its square, so that the observed and computed values that are to be compared are 2621, 3733, and 562, with 3149, 4517, and 1258 respectively for the three substances mentioned. The substitution of the former for the latter numbers in the formula will make a very great change indeed, and throw the observed and computed values of the refractive indices into hopeless disagreement.

If we are to retain the Sellmeier formula, only two methods of escape from these difficulties seem possible. One is to ascribe the discrepancies to experimental errors. This is, however, quite out of the question as regards the position of the absorption bands, and there is still less hope of reconciliation from the very slight differences in the measurements of the refractive indices. The greatest differences found in the refractive indices of rocksalt are those between the measurements of Langley, on the one hand, and Rubens, Nichols and Trowbridge on the other. The consequent changes in the estimates of  $K$  and  $\lambda_2^2$  from the Sellmeier formula, are, however, very slight, for, while Rubens gets  $K=5.179$  and  $\lambda_2^2=3149.3$ , Langley has  $K=5.175$  and  $\lambda_2^2=3145.7$ .

The other mode of escape that has been suggested is to ascribe the discrepancy between the observed and calculated values of  $\lambda_2$  to the influence of absorption bands in the unexplored regions. The Sellmeier formula contains a term  $c_n/(\lambda^2-\lambda_n^2)$ , corresponding to each absorption band, and one or more of these terms may be neglected in estimating the refractive index in any region, on the supposition that  $\lambda^2-\lambda_n^2$  is very large, which means, of course, that the region is far removed from the absorption bands in question. However, there is no evidence of the existence of any absorption band in a position that would enable us to bridge the gulf between theory and experiment for either rocksalt or sylvin.\* In the case of fluorite, there is a well-marked band in the neighbourhood of  $24\ \mu$  and strong absorption for a considerable distance beyond, but not reaching nearly so far as  $35.47\ \mu$ . The only one of the substances mentioned for which an absorption band has been found in a region that should affect the calculated refractive index is quartz. This has an absorption band at  $12.5\ \mu$ , which was not considered in the calculations quoted above. Quartz, however, is the substance in which the agreement between Sellmeier's formula and the observed values of the dielectric constant and the position of the other absorption bands is most satisfactory.

\* Quite recently Paschen has made another interesting contribution to the discussion of dispersion formulæ. In the 'Annalen der Physik' (1908, p. 120) he deals with rocksalt and sylvin on the basis of Sellmeier's formula. By assuming that there are three absorption bands—one in the infra-red and two in the ultra-violet—he has seven constants at his disposal, and obtains a close agreement between theory and observation as far as the dispersion is concerned. However, the difficulties as to the values of the constants in the formula do not seem to be removed. The dielectric constant is still too low, viz., 3.87, instead of 4.94, for sylvin, and 5.68, instead of 5.98, for rocksalt (taking the mean of the observations quoted above). The absorption bands of rocksalt are placed at  $0.12\ \mu$ ,  $0.16\ \mu$ , and  $60\ \mu$ , and those of sylvin at  $0.11\ \mu$ ,  $0.16\ \mu$ , and  $57\ \mu$ . Lyman has experimented with wave-lengths much less than  $0.16\ \mu$  without finding any absorption bands, and the most accurate observers of the bands in the infra-red agree in placing them a long way from  $60\ \mu$  and  $57\ \mu$ .

It seems then worth while inquiring whether there is not some other dispersion formula that will agree satisfactorily with the observed values of the refractive indices and be free from the difficulties in which Sellmeier's formula is involved. In order to make clear the meaning of the symbols, it may be well to sketch the process by which the formula that we propose to test may be derived.

Let  $\xi, \eta, \zeta$  denote the components of the displacement in an ether that resists rotations only. If, for convenience, we take the density of this ether to be unity, the torque  $F$  necessary to produce a rotation  $f$  is  $F = c^2 f$  and the work required to do this is  $\frac{1}{2} c^2 f^2$ . Here  $c^2$  is a coefficient of elasticity and  $c$  is the velocity of a wave in the ether. If there be electrons present, these will be disturbed so as to produce and equilibrate a new averaged rotational strain  $f'$ . The total rotation in the elastic ether is thus  $f + f'$ , say  $f_1$ , while the torque is  $F_1 = c^2 f$ . The quantity  $f'$  will, on the usual hypothesis of very small displacements, be proportional to  $f$ , so that we may write  $f' = (n^2 - 1)f$ , where  $n$  is some constant. We thus have  $F_1 = \frac{c^2}{n^2} f_1$ , where  $f_1 = n^2 f$ . The work absorbed in producing the total rotation  $f_1$ , for the compound medium made up of ether and electrons, will be  $\frac{1}{2} \frac{c^2}{n^2} f_1^2$ . Thus the  $c$  of free ether is replaced by  $c/n$  for the compound medium and  $n$  represents the refractive index. If we employ the language of electrodynamics,  $F$  is to be identified with the electromotive force and the velocity  $(\xi \ \eta \ \zeta)$  with the magnetic induction. In estimating the actual local electromotive force effective in straining any molecule  $P$  it is convenient, as in the theory of attractions, to consider separately the influence of the electrons within the region adjacent to  $P$  and that of the external field beyond this. What exactly the contribution of adjacent molecules is will depend on the character of the intermolecular forces and the configuration around each molecule; but in any case it must be proportional to  $f'$ , and it will be compensated locally by static reaction on the adjacent molecules. Hence the actual electromotive force around the molecule is

$$F' = c^2 (f + f' - a_1 f') = m f' (n^2 + a) / (n^2 - 1),$$

where  $m = (1 - a_1) c^2$  and  $a = a_1 / (1 - a_1)$ . We thus have

$$(n^2 - 1) / (n^2 + a) = m f' / F',$$

so that the refractive index ( $n$ ) depends on the relation between  $f'$  and the torque  $F'$  that produces it.

To find the relation between  $f'$  and  $F'$  we have to consider the effect on the molecule of the alternating field of force due to the impinging wave of light.

This is the well-known problem of determining the oscillations forced on a vibrating system in steady motion by a given periodic force. The principle of least action lends itself most readily to such a discussion and enables us to arrive at the form of the relation sought for without any special hypothesis as to the character of the steady motion of the electrons, or as to the nature of the intermolecular forces. If  $p/2\pi$  be the frequency of the impinging wave and  $\lambda$  the corresponding wave-length, we are thus led to the formula\*

$$\frac{n^2-1}{n^2+a} = \frac{mf'}{F'} = \frac{A_1}{p^2-p_1^2} + \frac{A_2}{p^2-p_2^2} + \dots + \frac{A_n}{p^2-p_n^2} \\ = \frac{B_1\lambda^2}{\lambda^2-\lambda_1^2} + \frac{B_2\lambda^2}{\lambda^2-\lambda_2^2} + \dots + \frac{B_n\lambda^2}{\lambda^2-\lambda_n^2},$$

where  $p_1/2\pi, \dots, p_n/2\pi$  are the frequencies of the free vibrations within the molecule. For indefinitely long waves we have  $n^2 = K$ , so that

$$\frac{K-1}{K+a} = B_1 + B_2 + \dots + B_n,$$

whence, by subtraction,

$$\frac{n^2-1}{n^2+a} = \frac{K-1}{K+a} + \frac{c_1}{\lambda^2-\lambda_1^2} + \frac{c_2}{\lambda^2-\lambda_2^2} + \dots + \frac{c_n}{\lambda^2-\lambda_n^2}.$$

This formula should give the refractive indices for all the different wave-lengths for which the medium is transparent. The formula will be modified in the same way as that of Sellmeier in the neighbourhood of an absorption band. If anything occurs to put  $f'$  out of phase with  $f$ , then  $p_1, \dots$  will be complex and there will be general absorption of the metallic type.

It has been remarked that the value of the constant  $a$  depends on the influence of the electrons in the immediate vicinity of the point where the disturbance is considered. In the present state of our ignorance as to the arrangement and mutual influence of the molecules the value of this constant cannot be accurately determined from theory. In the case of a liquid or gas we might expect the average effect to be that of a uniform distribution and under these circumstances Larmor† has given reasons for expecting the constant  $a$  to have the value 2. If  $a = 2$  we have the expression  $(n^2-1)/(n^2+2)$ , which is what occurs in Lorentz's original paper‡ connecting refractive index (and dispersion) with density. The experiments there discussed, and the more recent estimates of the refractive indices of liquids and gases agree, on the whole, fairly closely with Lorentz's

\* Cf. Larmor, 'Phil. Trans.,' 1897, A, p. 236, for an investigation in detail. What is here denoted by  $a$  is Larmor's  $4\pi/\lambda - 1$ .

† *Loc. cit.*, p. 233.

‡ H. A. Lorentz, 'Ann. der Physik u. Chemie,' 1879, vol. 9, p. 641.

theoretical formula. With these considerations before us it would seem natural to inquire whether the formula

$$\frac{n^2-1}{n^2+2} = \frac{K-1}{K+2} + \frac{c_1}{\lambda^2-\lambda_1^2} + \dots + \frac{c_n}{\lambda^2-\lambda_n^2}$$

will apply to solids as well as liquids. However, on attempting this on the basis of the experiments referred to below, we are met with the same difficulties that confronted us when considering Sellmeier's formula. A fair agreement between theory and observation can be obtained as far as the dispersion is concerned, but the constants are unsatisfactory. Thus in the case of rocksalt, if we take any probable value of the dielectric constant, the formula predicts an absorption band in the neighbourhood of  $46\mu$  and this is as much below the mark as that given by Sellmeier's formula is above it. We shall therefore retain the constant  $\alpha$  in our formula and endeavour to determine its value for different substances from the experimental evidence that is available.

The substance best adapted for the test of any such formula is rocksalt. Its refractive indices are known to a high degree of accuracy over a very large range, within which there are only two free periods as compared with four in the case of quartz. The addition of a free period increases the number of unknown constants, and makes it more difficult to determine any of them accurately.

Amongst the most careful determinations of the dispersion of rocksalt we have the observations of Langley\* from  $0.486\mu$  to  $4.123\mu$ , of Rubens† from  $0.434\mu$  to  $5.746\mu$ , of Paschen‡ from  $2.8\mu$  to  $9.76\mu$ , of Rubens§ from  $0.434\mu$  to  $8.95\mu$ , of Rubens and Nichols|| from  $0.434\mu$  to  $22.3\mu$ , and of Rubens and Trowbridge¶ from  $9.88\mu$  to  $17.87\mu$ . On the whole there is excellent agreement between these various observers, the differences in the estimates of the refractive indices being rarely more than 3 or 4 in the fifth significant figure. Langley gives the indices to seven significant figures, and his results are admirably self-consistent. Unfortunately, however, they are almost uniformly higher than those of the other observers, so that it is useless at present to include more than five figures in calculating the values of  $n$  from our formula. The influence of small differences in the fifth significant figure

\* 'American Journal of Science,' 1886, vol. 32, p. 98, and 'Annals of Astrophysical Observatory of Smithsonian Institution,' 1900, vol. 1, p. 261.

† 'Ann. der Physik u. Chemie,' 1892, vol. 45, p. 254.

‡ *Ibid.*, 1894, vol. 53, p. 340.

§ *Ibid.*, 1894, vol. 53, p. 278; and 1895, vol. 54, p. 482.

|| *Ibid.*, 1897, vol. 60, p. 454; and 'Physical Review,' 1897, vol. 5, p. 162.

¶ *Ibid.*, 1897, vol. 60, p. 733; and corrections in vol. 61, p. 224.

on the estimated values of the constants will, however, as has been indicated already, be very slight, and it is almost immaterial which set of observations we use as the basis of our computation.

If we take Langley's figures, our problem is to determine the six constants  $K$ ,  $a$ ,  $\lambda_1^2$ ,  $\lambda_2^2$ ,  $c_1$ , and  $c_2$ , from the formula

$$\frac{n^2-1}{n^2+a} = \frac{K-1}{K+a} + \frac{c_1}{\lambda^2-\lambda_1^2} + \frac{c_2}{\lambda^2-\lambda_2^2},$$

so as to get the best possible agreement with over 50 observations of the refractive index ( $n$ ) for different wave-lengths. To pick out six different observations and solve the corresponding set of six equations for the unknown constants would be possible but very laborious. After the eliminations were performed the resulting equations, of whatever degree, would have numerical coefficients, and so could be solved; but the process of elimination would be very troublesome. In practice it is more feasible to begin by trial and error, and to proceed by successive approximations. It soon becomes evident that the constant  $c_1$  is small, and that for large values of  $\lambda$  the term  $c_1/(\lambda^2-\lambda_1^2)$  is almost negligible compared with  $c_2/(\lambda^2-\lambda_2^2)$ . Thus for the longer wave-lengths we have the simpler formula

$$\frac{n^2-1}{n^2+a} = \frac{K-1}{K+a} + \frac{c_2}{\lambda^2-\lambda_2^2}.$$

Setting out, then, with any arbitrary values of  $a$  and  $K$ , we can determine the other constants to fit in with the experimental results, and proceed with this process until a set of values is reached that gives a close agreement throughout the whole range. Once such an agreement has been reached, we may reduce the equations for the small differences in the constants to a linear form by the process usual in such problems, and, if required, can determine the probable error of the various estimates.

It might seem at first that with so many constants at our disposal it would be possible to vary their values considerably without producing an appreciable change in the calculated values of the refractive indices. It will be found, however, on trial that the observations are sufficient to confine the constants within narrow ranges, and, amongst other things, that a slight diminution of the constant  $a$  would make  $\lambda_1^2$  negative, which is, of course, impossible. The process of trial and error described above leads to the following values of the constants:—

$\lambda_1^2 = 0.0160074,$	$\lambda_2^2 = 2632.14,$
$c_1 = 0.00191605,$	$c_2 = 683.816,$
$a = 5.51,$	$K = 5.9,$
$\lambda_1 = 0.12652,$	$\lambda_2 = 51.3.$



Calculating the refractive indices from the formula with these constants, we get the following table, which also gives a comparison with Langley's observations. The numbers obtained from theory and observation are identical except in the cases marked with an asterisk:—

$\lambda$ .	$n$ (theory).	$n$ (observation).	$\lambda$ .	$n$ (theory).	$n$ (observation).
0.4861 $\mu$	1.5533	1.5533	0.9916 $\mu$	1.5323	1.5323
0.4920	1.5526	1.5526	1.0084	1.5321	1.5321
0.4937	1.5525	1.5525	1.0368	1.5317	1.5317
0.4983	1.5519	1.5519	1.0540	1.5315	1.5315
0.5173	1.5500	1.5500	1.0810	1.5312	1.5312
0.5184	1.5499	1.5499	1.1058	1.5310	1.5310
0.5273	1.5491	1.5491	1.1420	1.53069	1.53063*
0.5372	1.5482	1.5482	1.1780	1.5303	1.5303
0.5530	1.5469	1.5469	1.2016	1.53018	1.53014*
0.5660	1.54586	1.5458*	1.2604	1.5297	1.5297
0.5710	1.5455	1.5455	1.3126	1.5294	1.5294
0.5758	1.5452	1.5452	1.4874	1.5285	1.5285
0.5786	1.5450	1.5450	1.5552	1.52820	1.52814*
0.5860	1.5445	1.5445	1.6368	1.5278	1.5278
0.5893	1.5443	1.5443	1.6848	1.52770	1.52764*
0.6105	1.5430	1.5430	1.7670	1.5274	1.5274
0.6400	1.5414	1.5414	2.0736	1.5265	1.5265
0.6563	1.5406	1.5406	2.1824	1.5263	1.5262*
0.6874	1.5393	1.5393	2.2464	1.5261	1.5261
0.7190	1.53814	1.53815*	2.3560	1.5258	1.5258
0.7604	1.5368	1.5368	3.1104	1.5241	1.5240*
0.7992	1.5358	1.5358	3.2736	1.5237	1.5237
0.8424	1.5348	1.5348	3.3696	1.5235	1.5235
0.8835	1.5340	1.5340	3.6288	1.5229	1.5229
0.9033	1.5336	1.5336	3.8192	1.5224	1.5224
0.9724	1.5325	1.5325	4.1230	1.5216	1.5216

The differences between theory and observation being so slight, and in every case less than those between the different observers, it was not thought necessary to proceed to any closer approximation by modifications of the constants.

We must now inquire how the refractive indices obtained from our formula with these constants agree with the observations of Rubens and others in the region beyond 4.123  $\mu$ . The results are set out in the following table:—

$\lambda$ .	$n$ (theory).	$n$ (observation).	Difference.
4.65 $\mu$	1.5200	1.5197	+0.0003
5.22	1.5183	1.5180	+0.0003
5.79	1.5155	1.5159	-0.0004
6.78	1.5123	1.5121	+0.0002
7.22	1.5103	1.5102	+0.0001
7.59	1.5086	1.5085	+0.0001
8.04	1.5063	1.5064	-0.0001
8.67	1.5030	1.5030	0
9.95	1.4952	1.4951	+0.0001
11.88	1.4809	1.4805	+0.0004
13.96	1.4625	1.4627	-0.0002
15.89	1.4415	1.4410	+0.0005
17.93	1.4152	1.4148	+0.0004
20.57	1.3736	1.3735	+0.0001
22.3	1.3407	1.3403	+0.0004

It will be seen that the agreement is very close throughout, the differences being nearly all of the order of experimental error. In considering the slight differences that do exist, we must bear in mind two facts. (1) The formula, with the constants adopted, gives values of  $n$  for the larger wave-lengths that are on the average slightly in excess of those observed. This is what is to be expected from the fact that the constants were chosen to fit in with Langley's observations, and in the range common to all observers Langley's results are almost uniformly slightly higher than those of the others. (2) For the larger wave-lengths an error in the estimate of  $\lambda$  affects the refractive index more than in the case of short waves. Thus in the neighbourhood of  $18\mu$  an error of one-sixth of 1 per cent. in the estimate of the wave-length would account for a difference of more than 0.0004 in the value of the refractive index. Such a mistake in the estimate of the wave-length is not beyond the limits of experimental error in this region.\*

The value of  $\lambda_1$  adopted to fit in with Langley's observations of the refractive indices is  $\lambda_1 = 0.12652\mu$ . If we had used the observations of Rubens instead of those of Langley we should have found a slightly lower value of  $\lambda_1$ . We should thus expect an absorption band in the neighbourhood of  $0.12\mu$ . Lyman, in his examination of rocksalt, used wave-lengths as short as  $0.125\mu$ . He did not find an absorption band, but he discovered marked absorption for the shorter wave-lengths, indicating that he was on the confines of a band.†

It thus appears that the formula

$$\frac{n^2-1}{n^2+a} = \frac{K-1}{K+a} + \frac{c_1}{\lambda^2-\lambda_1^2} + \frac{c_2}{\lambda^2-\lambda_2^2}$$

is in thorough accord with experimental knowledge on the optical properties of rocksalt. It agrees with experiment in indicating absorption bands in the neighbourhood of  $0.12\mu$ , and of  $51.3\mu$ ; it suggests a dielectric constant of 5.9, which is very near the mean of the best experimental measurements of that constant; and it assigns values to the indices of refraction agreeing within the limits of experimental error with 70 observations extending over nearly six octaves.

Next to rocksalt, the substance for which the existing data are best adapted for the test of a dispersion formula such as that here discussed is fluorite. Its refractive indices have been carefully determined from  $0.198\mu$

\* See Rubens and Nichols, 'Physical Review,' 1897, vol. 5, pp. 102 and 161; and 'Ann. der Phys. u. Chemie,' 1897, vol. 60, pp. 426 and 453.

† 'Astrophysical Journal,' Jan., 1907, pp. 51 and 52.

to  $8.95\mu$  by Rubens and Snow,\* from  $0.1856\mu$  to  $9.4291\mu$  by Sarasin, Carvallo and Paschen,† from  $0.2\mu$  to  $2.34\mu$  by Simon,‡ and from  $0.76\mu$  to  $3.4\mu$  by Langley.§

Taking the numbers as set out by Paschen as the basis of our calculations, we get the following approximate values of the constants in the dispersion formula:—

$$\begin{aligned} a &= 1.04, & K &= 6.8, \\ \lambda_1^2 &= 0.00716764, & \lambda_2^2 &= 576.353, \\ \lambda_1 &= 0.0846618, & \lambda_2 &= 24.0074, \\ c_1 &= 0.001303, & c_2 &= 231.856. \end{aligned}$$

The corresponding values of the refractive indices for different wavelengths are set out below, with a comparison between theory and observation.

$\lambda$ .	$n$ (experiment).	$n$ (theory).	Difference.
0.1856	1.5094	1.50945	+0.00005
0.19881	1.4963	1.4962	-0.0001
0.20243	1.4933	1.4932	-0.0001
0.20610	1.4904	1.4904	0
0.20988	1.4876	1.4875	-0.0001
0.21441	1.4846	1.4845	-0.0001
0.22645	1.4776	1.4775	-0.0001
0.23125	1.4752	1.4751	-0.0001
0.25718	1.4648	1.4647	-0.0001
0.27467	1.4596	1.4596	0
0.32525	1.4499	1.4498	-0.0001
0.34015	1.4477	1.4477	0
0.34655	1.4470	1.4469	-0.0001
0.36009	1.4454	1.4454	0
0.39685	1.4421	1.4419	-0.0002
0.48607	1.4371	1.4371	0
0.58932	1.4339	1.4339	0
0.65618	1.4326	1.4327	+0.0001
0.68671	1.4320	1.4320	0
0.71836	1.4316	1.4317	+0.0001
0.76040	1.4310	1.4311	+0.0001
0.8840	1.4298	1.4299	+0.0001
1.1786	1.4279	1.4280	+0.0001
1.3756	1.4269	1.4270	+0.0001
1.4733	1.4264	1.4265	+0.0001
1.5715	1.4260	1.4261	+0.0001
1.7680	1.4251	1.4251	0
1.9153	1.4244	1.4244	0
1.9644	1.4241	1.4241	0
2.0626	1.4236	1.4237	+0.0001
2.1608	1.4231	1.4231	0
2.3573	1.4220	1.4220	0
2.5537	1.4209	1.4209	0
2.6519	1.4202	1.4202	0

\* 'Ann. der Phys. u. Chem.,' 1894, vol. 53, p. 273; 1892, vol. 45, p. 254; 1892, vol. 46, p. 529.

† *Ibid.*, 1894, vol. 53, p. 328; 1895, vol. 56, pp. 765 and 821.

‡ *Ibid.*, vol. 53, p. 553.

§ 'Annals of Astr. Obs.,' vol. 1, p. 221; see also Martens, 'Ann. der Phys.,' vol. 6, 1901, p. 619.

$\lambda$ .	$n$ (experiment).	$n$ (theory).	Difference.
2·9466	1·4183	1·4183	0
3·2413	1·4161	1·4161	0
3·5359	1·4138	1·4138	0
3·8306	1·4112	1·4112	0
4·1252	1·4085	1·4085	0
4·7146	1·4024	1·4023	-0·0001
5·3036	1·3953	1·3952	-0·0001
5·8932	1·3872	1·3871	-0·0001
6·4825	1·3782	1·3781	-0·0001
7·0718	1·3680	1·3680	0
7·6612	1·3568	1·3568	0
8·2505	1·3444	1·3444	0
8·8398	1·3308	1·3308	0
9·4291	1·3161	1·3161	0

It will be seen that the agreement is very close throughout. It could probably be improved by a slight modification of the constants in the dispersion formula; but it is needless to do this until there is a closer agreement between different observers as to the values of the refractive indices.

The value assigned to the dielectric constant is the mean of the best direct determinations of that quantity, and the prediction as to the positions of the absorption bands is as near the mark as could be desired.

*The Effect of Pressure upon Arc Spectra.* No. 2.—Copper,  
 $\lambda$  4000— $\lambda$  4600.

By W. GEOFFREY DUFFIELD, D.Sc.

(Communicated by Professor E. Rutherford, F.R.S. Received September 1, 1908.)

(Abstract.)

A direct current arc from 100-volt mains was formed between copper rods within a pressure cylinder designed by Professor J. E. Petavel, F.R.S. The light passed through a glass window, and, after reflection from two mirrors, was focussed upon the slit of the large Rowland grating spectroscope in the Physical Laboratories of the Manchester University. The apparatus and method of using it have been described in a previous paper.\*

The spectrum of the copper arc in air has been photographed in the region  $\lambda = 4000$  to  $\lambda = 4600$  Å.U. at the following pressures: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 100, 125,† 150,† 203† atmospheres (excess above 1 atmosphere).

*I. Broadening.*

Within the region  $\lambda\lambda$  4000—4600 :—

1. All lines are broader under high pressures than under atmospheric pressure.

2. The broadening increases with the pressure; it has not been determined if the increase is continuous and linear with the pressure.

3. The broadening of all lines is unsymmetrical, being greater on the red side.

4. The amount of broadening is different for different lines.

5. Two types of broadening have been observed: some lines at first become faint and hazy, almost resembling bands, and are completely dissipated under higher pressures (series lines); others, though much broadened, remain well-defined lines (non-series lines).

6. No simple relation has been found between the width of a line under pressure and its original intensity.

7. The intensity curves of the sharp lines under pressure are steeper towards the violet than are those of the nebulous lines. The sharp and nebulous lines retain their characteristic "hard" and "soft" appearances throughout.

\* Duffield, 'Phil. Trans.,' A, vol. 208, p. 111 (1908).

† Added October 19, 1908.—G. D.

8. The nebulous and sharp non-series lines broaden to about the same extent; for the well-defined lines, the width may be as great as 12 Å.U. at 203 atmospheres.\*

9. The broadening at first appears to increase more rapidly than the displacement, making measurements at low pressures less accurate than those at high pressures.

## II. *Displacement.*

Within the region  $\lambda\lambda$  4000—4600 :—

1. Under pressure, the most intense portion of every line is displaced from the position it occupies at a pressure of 1 atmosphere.

2. The displacement is in the direction of greater wave-length.

3. The displacement is real, and not due to unsymmetrical broadening, *i.e.*, the line is broadened about a displaced position.

4. The displacement of each line is, within the limits of accuracy of the experiments, continuous and linear with the pressure.

5. The rates of increase of the displacement with the pressure are different for different lines.

6. The lines belonging to the first and second subordinate series have greater displacements than the non-series lines. Their great width precludes accurate measurement.

7. The displacements of non-series lines are functions of their wave-lengths. The evidence indicates that they vary with a power of the latter, at least as great as the third and possibly as great as the sixth.

8. There is some reason to believe that there are two values for the displacement of a line at one and the same pressure.

9. The mean displacement of the non-series lines is 12.2-thousandths of an Å.U. per atmosphere. The largest displacement measured is a little more than 2 Å.U. at 203 atmospheres.\*

## III. *Reversals.*

None of the copper lines within this region showed any signs of reversal under pressure.

## IV. *Relative Intensities.*

Within the region  $\lambda\lambda$  4000—4600 :—

1. Changes in relative intensities of lines occur under pressure.

2. Those belonging to either the first or second subordinate series vanish at

\* Added October 19, 1908,—G. D.

about 40 atmospheres and do not reappear as the pressure is increased (obliterated lines).

3. Members of the first sub-series become at low pressures faint and hazy, almost resembling bands, and are at higher pressures dissipated. There is, however, always a marked cloudiness in the neighbourhood of their original position.

4. Members of the second sub-series gradually diminish in intensity without abnormal widening. No cloudiness is distinguishable near their original position.

5. Of the non-series lines, those that are nebulous are strengthened relatively to those that are sharp.

6. Lines strengthened under pressure do not correspond with those given by other workers as "enhanced" lines.

#### *V. Brightness of the Arc.*

The brightness of the copper arc increases enormously with the pressure of the surrounding air.

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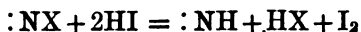
*The Action of Chlorine upon Urea whereby a Dichloro Urea is produced.*

By FREDERICK DANIEL CHATTAWAY, F.R.S.

(Received June 10,—Read June 25, 1908.)

Although a few of the more familiar substances containing halogen attached to nitrogen, as, for example, nitrogen chloride, have been known for a long period, it is only within the last 10 years that such compounds have been systematically studied. They form, however, a group of extraordinary interest and play an all important part in many complex reactions; to illustrate this it is only necessary to refer to the substitution of halogen in anilides and to the well-known method for obtaining amines from amides. I have shown in a series of investigations that hydrogen attached to nitrogen in compounds of the most varied characters may be replaced with ease by chlorine or bromine if suitable conditions are observed and it may be said, speaking generally, that this can always be done, although the nitrogen halogen derivatives produced may react or undergo isomeric change so readily that they can only with difficulty be isolated.

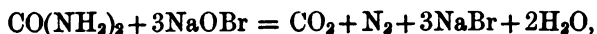
All compounds in which halogen is directly attached to trivalent nitrogen can take part in certain well-defined reactions characteristic of the linkage. One of the most striking of these group reactions is that with hydriodic acid, whereby at the ordinary temperature the halogen is replaced by hydrogen and iodine is liberated quantitatively. This reaction, which may be expressed by the general equation



affords an easy method of analysing these compounds.

Such a nitrogen halogen derivative is formed as an intermediate product in a reaction with urea, the course of which has never hitherto been explained although it has received an unusual amount of attention on account of its furnishing a ready method of estimating the quantity of this substance present in a liquid.

When urea is added to a solution of an alkaline hypochlorite or hypobromite it is at once decomposed, nitrogen and carbon dioxide being set free; if an excess of alkali is used the carbon dioxide is fixed and the nitrogen, which alone escapes, should thus afford a measure of the amount of urea. The reaction is generally represented by the equation:—

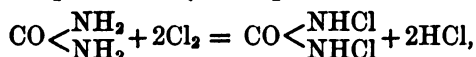




which throws no light upon its nature; indeed it obscures it, as it makes it appear to be a case of oxidation. It does not even express quantitatively what takes place, for all chemists who have investigated the decomposition have noted that the amount of nitrogen liberated is invariably less than that contained in the urea used. When the operations are carried out under specified conditions this loss of nitrogen, which may amount to as much as half of the total, is very constant and so can be allowed for by adding a definite fraction of the whole to the gas actually measured. The method can thus be made to give results sufficiently accurate for clinical purposes and since it is easy to carry out it has received very general application. It is not known what becomes of the nitrogen which does not appear as gas, for all the suggestions that have been made hitherto wholly fail to account for more than a small fraction of the quantity that disappears.

If urea be added instead of to an alkaline solution of a hypochlorite to one acidified by acetic acid, that is to a solution of hypochlorous acid no gas is evolved, nor is any gas liberated if chlorine itself is passed into a solution of urea in acetic acid. Action, however, takes place in each case and a nitrogen chloride is produced; for although the hypochlorous acid or chlorine disappears, the resulting solution liberates iodine in large quantity from hydriodic acid.

The isolation of the substance produced from such a solution is not practicable, since the method of extraction by chloroform which often serves for the separation of substituted nitrogen chlorides cannot be used, as the chloro urea formed is easily soluble in water but almost insoluble in chloroform. It is, however, less soluble in water than urea itself and crystallises out in a pure condition when chlorine in excess is passed rapidly through a cooled sufficiently strong aqueous solution of urea. The action which takes place is represented by the equation



two only of the four hydrogen atoms of the urea being replaced by chlorine.

This dichloro derivative appears to be the only stable nitrogen chloride which urea is capable of forming. The crystals which separate from the solution of urea have this composition from the first and chlorine seems to have no further substituting action upon them.

Dichloro urea, having regard to its mode of formation, as well as to the structure of urea itself, has most probably the constitution represented by

the formula  $\text{O}:\text{C} \begin{smallmatrix} \text{N} < \text{Cl} \\ & \text{H} \\ \text{N} < \text{Cl} \end{smallmatrix}$ , which explains its formation and such of its

reactions as have yet been studied.

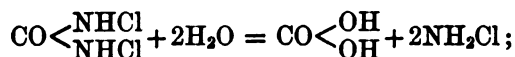
If this constitution be granted it seems probable that the reaction between urea and chlorine takes place in two stages and that the amino groups are substituted successively, but the monochloro derivative does not crystallise out, possibly owing to its solubility being not far removed from that of urea itself. Either of two causes may prevent the formation of a ter- or tetrachloro derivative; the hydrochloric acid which is formed in the reaction may prevent that addition of chlorine to the nitrogen which must precede further substitution, or the more highly substituted urea may be hydrolysed so easily that it breaks up as soon as it is formed. Dichloro urea is so much more easily hydrolysed than urea itself that the latter is the more probable cause.

Although two molecules of hydrogen chloride are formed when urea is substituted by chlorine, very little heat is developed, dichloro urea must therefore be an endothermic compound and might be expected to be highly explosive. When heated, however, it does not explode itself but decomposes with liberation of nitrogen chloride which, if heated a few degrees above the temperature at which it is set free, may detonate with great violence.

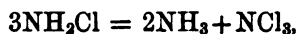
Dichloro urea gives all the characteristic reactions of a typical nitrogen chloride; for instance, it liberates iodine from hydriodic acid, chlorine from hydrochloric acid, and reacts with alcohol, forming ethyl hypochlorite, urea being in each case re-formed.

It is distinguished from most other substituted nitrogen chlorides by the readiness with which it is hydrolysed in presence of water, nitrogen chloride, carbon dioxide, a little nitrogen and ammonium chloride being formed. If the compound is dissolved in water or kept in a moist atmosphere, this hydrolysis takes place slowly at the ordinary temperature and becomes very rapid at about 30° C.

It is probable that in this reaction a mono-substituted ammonia is first produced thus:—



but if so it apparently can only exist momentarily, as nitrogen chloride is at once liberated. The formation of the end products of the reaction can be explained by assuming that this monochloro ammonia at once breaks up into ammonia and nitrogen chloride,

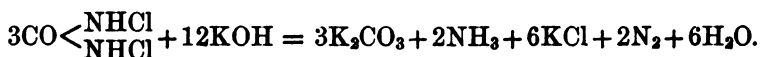


which then to some extent react, forming nitrogen and hydrogen chloride, the latter at once combining with the free ammonia and allowing the remaining

nitrogen chloride to escape, as this does not react with ammonium chloride. Both acids and alkalis accelerate the rate of hydrolysis and also alter the nature of the end products by hindering or furthering the secondary reaction between the ammonia and the nitrogen chloride.

In presence of dilute acids the ammonia is at once fixed and the reaction between it and the nitrogen chloride with its accompanying liberation of nitrogen is prevented, all the chlorine contained in the dichloro urea is therefore liberated as nitrogen chloride. In presence of alkalis, on the other hand, the reaction between the ammonia and the nitrogen chloride goes on to completion, since the hydrochloric acid formed in it is at once fixed; no nitrogen chloride, therefore, is set free, since twice as much ammonia is formed as is required to decompose it.

The reaction between dichloro urea and a solution of caustic potash is instantaneous: nitrogen is liberated with violent effervescence, the excess of ammonia and the alkaline carbonate formed remaining dissolved in the liquid. The action, which is quantitative, is expressed by the equation



The behaviour of dichloro urea with alkalis affords an explanation of the course of the reaction which occurs when urea is decomposed either by an excess of alkaline hypochlorite or hypobromite. The urea is, without doubt, converted into dichloro or dibromo urea,\* which is at once hydrolysed in the manner above described. In presence of the excess of hypochlorite or hypobromite, the mono-substituted ammonia formed in the hydrolysis may be further substituted to a greater or less extent, nitrogen being evolved quantitatively only when this takes place under such conditions that the amount of hydrogen attached to nitrogen in the reacting system is always sufficient to react completely with the chlorine attached to nitrogen.

*Preparation of Dichloro Urea.*—The preparation of dichloro urea should be carried out at a low temperature and as rapidly as possible, since, in presence of the hydrochloric acid formed at the same time, hydrolysis so readily occurs and so much nitrogen chloride is produced that if it is carried out at the ordinary temperature, or its duration is unnecessarily prolonged, a poor yield is obtained. It is best, therefore, to work with small quantities, to cool thoroughly, and to pass the chlorine as rapidly as possible.

\* It is possible that in absence of free acid, and in presence of excess of hypochlorite or hypobromite, a tri- or tetra- substitution product may be produced, the formation and decomposition of which can be formulated easily, but this does not affect the essential character of the reaction, which is one of halogen substitution followed by hydrolysis of the substituted urea and interaction between the resulting compounds.

The following procedure gives a good result:—Dissolve 20 grammes of urea in 40 c.c. of water and cool to about  $-10^{\circ}$  C. in a mixture of alcohol and crushed ice.\* Pass in as rapidly as practicable a stream of chlorine made by dropping strong hydrochloric acid upon bleaching powder. So little heat is evolved in the reaction that with proper cooling the temperature never rises above zero, however rapid the stream of chlorine. Nitrogen chloride is produced from the first and can be recognised by its characteristic smell, but it remains in solution, the liquid, owing to its presence, becoming bright yellow in colour. After passing the chlorine for a considerable time, white crystals make their appearance, at first usually on the surface of the liquid; these increase in amount till the whole becomes a pulp of thin colourless plates. When these no longer appear to increase in amount, filter off, separating the acid mother liquor as completely as possible; wash once or twice with a little water and when as much of the latter as possible has been removed wash the crystals several times with dry chloroform. Dichloro urea is not appreciably soluble in cold chloroform and a good deal of adhering moisture is thus got rid of. Press finally between filter paper, spread out in a thin layer on a clock glass, and free from the last traces of water by exposing for about half an hour over phosphoric oxide in a vacuum.

A further crop of crystals can be obtained by again passing chlorine through the cooled mother liquor and this can be repeated as long as any separate. Nothing besides dichloro urea and the products of its hydrolysis are formed in the reaction; if the acid mother liquor is evaporated down, carbon dioxide is given off and nitrogen chloride escapes in quantity; later, as the liquid becomes concentrated, hydrogen chloride is expelled, and finally ammonium chloride is left.

Although the final result of the action which takes place is the substitution of two atoms of hydrogen by two atoms of chlorine, as in other similar cases, this is without doubt effected by the addition of four atoms of chlorine to the nitrogen followed by the elimination of two molecules of hydrogen chloride.

The yield of dichloro urea is not very large, so much being hydrolysed during the process: in a well conducted experiment it reaches about 25 per cent. of the theoretical, the weight of pure dry product obtained amounting as a rule to rather more than half the weight of the urea used. The loss, although largely due to the hydrolysis of the compound, is much increased by the

\* It is not absolutely necessary to use a freezing mixture, the temperature, owing to the urea dissolving, falls at once to below zero, and if the flask in which the operation is carried out is cooled by tap-water, a moderate amount of the compound can be obtained, but the yield is much better at a lower temperature.

circumstance that dichloro urea is very soluble in water and consequently a considerable amount does not crystallise out from the mother liquor.

Dichloro urea reacts with an aqueous solution of hydriodic acid in the way characteristic of nitrogen chlorides; urea is reformed and iodine quantitatively liberated. It was analysed by taking advantage of this reaction: a known weight was added to an excess of a solution of potassium iodide made acid by acetic acid and the iodine liberated estimated by a standard solution of sodium thiosulphate.

0.5112 gramme liberated iodine = 158.6 c.c. N/10 I.

Cl, as : NCl = 54.99 per cent.

CON<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> requires Cl, as : NCl = 54.96 per cent.

Dichloro urea cannot be kept for any length of time without change. When damp it hydrolyses exactly as when dissolved in water. To obtain it pure, therefore, it must be dried very rapidly over phosphoric oxide in a vacuum. When only freed from adhering water as far as possible by a pump, it is slowly hydrolysed by the retained moisture even though placed in a desiccator over strong sulphuric acid, and this often occurs to such an extent that the mass becomes quite yellow from the nitrogen chloride mechanically retained by the crystals. To show the amount of hydrolysis which takes place under these conditions a quantity of the pure substance freed from all but adhering water thus was kept over strong sulphuric acid, and analysed from time to time, the nitrogen chloride formed being allowed occasionally to escape. In two days the percentage of chlorine as : NCl had fallen to 43.79 and in seven days to 13.33.

Even when dried and kept over phosphoric oxide it slowly decomposes, nitrogen chloride being evolved. A quantity of the pure dry compound thus preserved in a vacuum over phosphoric oxide was analysed at intervals; after 12 hours the percentage of Cl as : NCl had fallen to 54.67, after two days to 52.97, and after nine days to 47.87 per cent.

When an aqueous solution is kept at the ordinary temperature the dichloro urea is slowly hydrolysed; carbon dioxide, a little nitrogen and nitrogen chloride escape and ammonium chloride remains in solution. Hydrolysis by water takes many days to complete unless the aqueous solution is warmed, when it is much more rapid; at about 20° bubbles of gas are freely evolved and rapid effervescence sets in at about 40°, the nitrogen chloride escaping without explosion.

Dichloro urea prepared as described above is a soft, white, crystalline powder with a pearly lustre. Under the microscope it is seen to consist of thin transparent plates somewhat irregular in shape. It can be recrystallised

from water, in which it is easily soluble and from which it separates in similar but larger plates, by cooling an aqueous solution saturated at about  $15^{\circ}$  C. though with some loss owing to hydrolysis. Its aqueous solution is at first colourless but becomes yellow as hydrolysis proceeds, owing to the liberation of yellow nitrogen chloride which remains dissolved in the water. It is easily soluble in alcohol and ether, very slightly soluble in chloroform and insoluble in petroleum ether. When its alcoholic solution is heated it reacts in the way characteristic of nitrogen chlorides, urea is reformed and ethyl hypochlorite is produced, the latter very easily breaking down into aldehyde and hydrogen chloride.

Its behaviour with acids is complicated by the circumstance that it is so readily hydrolysed; for example, when it is added to strong hydrochloric acid though chlorine is rapidly given off the amount of urea reformed is not very large. When placed in cold strong sulphuric acid it is hydrolysed and nitrogen chloride is liberated. The latter decomposes into its elements if the liquid be heated, its characteristic smell disappearing and being replaced by that of chlorine.

Dichloro urea is a compound of a marked acid character, it has an acid taste recalling that of hypochlorous acid and its aqueous solution strongly reddens litmus paper, which only becomes bleached after the lapse of some minutes. It acts very corrosively upon the skin, staining it yellow and destroying the tissues.

When heated, dichloro urea melts with decomposition at about  $83^{\circ}$ , nitrogen chloride being liberated. Although the substance appears not itself to explode, if the temperature of the bath in which the melting point is being taken is allowed to rise at all rapidly a few degrees above this point, the nitrogen chloride set free in the melting point tube may explode with considerable violence.

It can be decomposed without danger by throwing it into a porcelain dish heated to  $100^{\circ}$  on a water bath in quantities of not more than about half a gramme at a time. The white compound fuses and gives off nitrogen chloride as a yellow vapour which escapes quietly unless, through too large a quantity of material having been decomposed at once, some of the vapour is mechanically retained as bubbles in the semi-fused residue and thus becomes heated to the temperature at which it explodes. Hydrogen chloride is not set free when dichloro urea is thus decomposed by heat.

When an aqueous solution of the compound is added to a solution of caustic soda, vigorous effervescence, due to escape of nitrogen, occurs. The liquid remaining contains ammonia and potassium carbonate, the volume of carbon dioxide liberated when this is treated with an acid being to the volume of

nitrogen previously liberated in the ratio of 3 to 2. One-third of the nitrogen contained in the dichloro urea used is found as ammonia.

The investigation of dichloro urea, which is an extremely reactive body and promises to be of considerable use in organic synthesis, is being continued.

The thanks of the author are due to Dr. Baker for allowing him to use the Christ Church Laboratory, where this work has been carried out.

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*Note on the Instability of Tubes subjected to End Pressure, and  
on the Folds in a Flexible Material.*

By A. MALLOCK, F.R.S.

(Received and read June 25, 1908.)

When a straight rod is subjected to end compression it is stable for small lateral displacements unless the compressing force exceeds a definite limit depending on the elastic constants of the material of the rod and its length and cross section dimensions.

If this limit is exceeded, the rod is unstable and the least departure from straightness grows under the action of the force, the axis of the rod then taking the form of one of the well-known elastic curves; and this is the only form which a solid rod can take in the circumstances.

With tubes and plates, however, the case is different, for with the tube the ratio of the thickness of the walls to the diameter of the tube has to be considered as well as the ratio of the diameter to the length. Thus a tube whose length is insufficient to produce instability involving a bending of the axis may become unstable by the crumpling up of the walls, the axis itself remaining straight.

In plates something of the same kind may take place. The edges of a rectangular plate may be constrained to remain straight and parallel to one another, but if pressure is applied to two opposite edges instability will ensue if it exceeds a critical value.

In the case of solid rods the governing condition is the constancy (to the first order) of the length of the axis; with tubes and plates it is the constancy to the same order of the area of the mid-wall surface. Considering the case of tubes in rather more detail, take the axis of the tube as  $z$  and let its unstrained radius be  $r_0$ .

Under end compression the surface may become unstable by deformation into any of the cylindrical harmonics of the type

$$r = r_0 + a \cos n \theta \cos \frac{2\pi}{\lambda} z,$$

where  $\theta$  is the angle which  $r$  makes with a fixed diameter of the tube and  $\lambda$  the length of the fold parallel to the axis. The order of the harmonic which will naturally be assumed by the deformed tube depends on the ratio ( $h/r$ ) of the thickness of the walls to the diameter and will be such that the potential energy of the combined bending and shearing involved may be a maximum.

I will not in this note work out individual cases, but it will be seen that the smaller the ratio  $h/r$  the higher will be the order of the harmonic, because, since the shear becomes relatively more important as  $h/r$  diminishes,  $\lambda/r$  must also diminish to fulfil the condition of maximum potential energy.\*

If the crushing is continued until the tube is greatly reduced in length the folds are seen to develop into the symmetrical shapes shown in the photographs (figs. 1, 2, 3), for which  $n = 1, 2$ , and  $3$  respectively. For  $n = 1$  the folds



FIG. 1.

FIG. 2.

FIG. 3.

are circular in plan and independent of  $\theta$ ; when  $n = 2$  the plan of the folds is a square, and when  $n = 3$  the plan is hexagonal.

It may be noticed that the instability always shows itself first at one end, and that since the reaction against end pressure decreases as the deformation goes on, each fold is completed in succession, the next not becoming marked until the reaction is increased by the previous fold resting against the last but one.

\* It often happens that owing to the constraint applied by the surfaces between which the tube is crushed, the fold first formed is of the first order, even when the ratio of thickness to diameter is such that a higher order is the natural one.



The crushing force requisite therefore undergoes periodic variations, being a maximum at the beginning of the formation of a new fold and a minimum when the fold is nearly completed.

If we examine the completed folds on the assumption that the extension of any element of the surface is small compared to the depth of the fold, it will be seen that the side of each fold (AB), see fig. 4 (for which  $n = 3$ ), at the

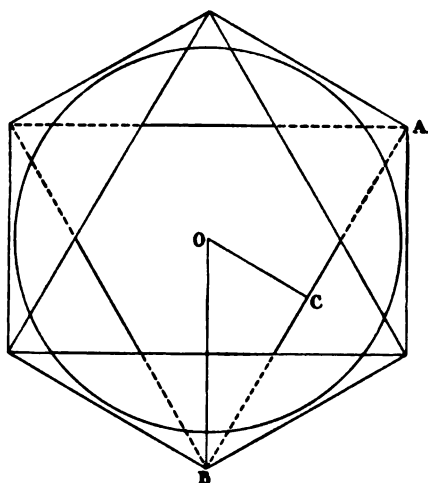


FIG. 4.

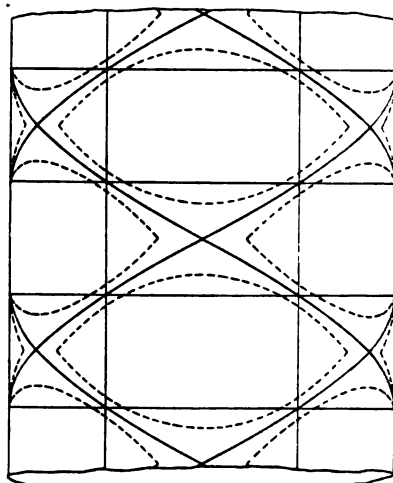


FIG. 5.

re-entrant angle has a length  $2\pi r/n$ . Also that the least distance (OC) of the fold from the centre is  $\frac{\pi r}{n} \cos \frac{\pi}{n}$  and the maximum distance (OB) is  $\frac{\pi r}{n} \sin \frac{\pi}{n}$ . The length of each fold as it would appear on the undeformed tube is therefore  $2\pi r (1 - \cos \frac{\pi}{n}) n \sin \frac{\pi}{n}$ . Thus for  $n = 2$ ,  $\lambda = \pi r$ ; and for  $n = 3$ ,  $\lambda = 2\pi r/3\sqrt{3}$ . The formulæ do not apply when  $n = 1$ , for in this case the assumption that the extension is small compared to the depth of the fold is untenable. But with  $n = 2$  and  $n = 3$  I find by trial that the number of folds formed from a given length of tube corresponds very fairly with the supposition that the extension is small.

In fig. 5 the vertical and horizontal lines are the nodal lines of the harmonic  $\cos 3\theta \cos 3\sqrt{3}z$  on a cylindrical surface; the spiral lines ultimately become the salient angles of the folds, and the dotted lines indicate the locus of points of no compression or extension when the tube is completely crushed.

The potential due to small deformations of either the tubular or the completely crushed surface can be calculated by the use of recognised

functions, but the intermediate stages, where the local extension or compression of the mid-wall surface is not a small quantity, present a far more difficult problem, the solution of which would probably require the investigation of functions of a new class.

The problem is, in fact, merely a particular case of the general theory of the form of the folds of drapery, that is of the surfaces into which a plane can be deformed if its material can be stretched by an amount which is finite but small compared to the depth of the folds.

As a simple example, consider the case of a circular cone (fig. 6). Let this

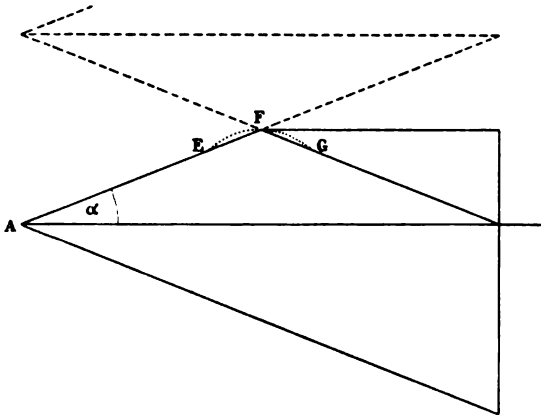


FIG. 6.

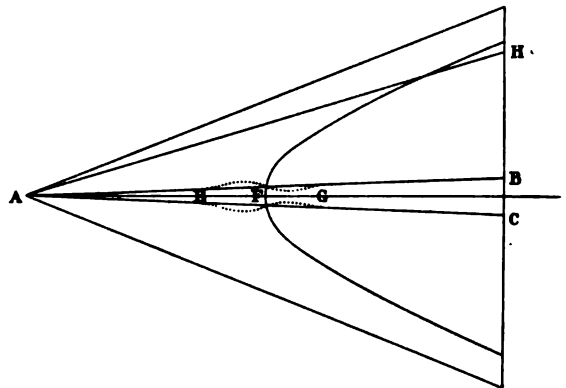


FIG. 7.

be intersected by a similar cone, the axes of both being in the same plane, and intersecting at equal distances from their apices. The curve of the intersection of the surfaces is a conic whose plane bisects the angle between the axes. Now let that part of one of the cones outside the curve of intersection be removed; the remaining surface is of exactly the same area as the original cone and could have been formed from it by bending without any stretching of the mid-surface. Such a partly inverted cone is typical of the fold in a flexible and inextensible surface, and it remains to be seen what form the angle of the fold would take if the material resisted bending. In this case there cannot be an abrupt change in the direction of the surface in passing from the original cone to the part inverted, and what in the perfectly thin and flexible material was a sharp crease becomes, in virtue of the stiffness, a rounded curve, EFG.

If AB, AC, fig. 7, are two of the generating lines of the cone, a small distance on either side of that passing through the vertex of the conic, the effect of resistance to bending will be to increase the distance of the surface from the axis of the original cone from E to F and to diminish the distance

of the surface from the axis of the inverted cone from F to G. Hence there will be circumferential extension of the material from E to F and circumferential compression from F to G.

The distorted generating lines will therefore take some such shape as is indicated by the dotted lines in fig. 7.

In the undistorted cones the principal radii of curvature at the vertex of the conic are, for the original cone,  $-\infty$  and  $AF \tan \alpha$  and for the inverted surface  $+\infty$  and  $-AF \tan \alpha$ . By a general theorem relating to the curvature of surfaces (the measure of curvature being  $(R_1 R_2)^{-1}$ , where  $R_1 R_2$  is the product of the principal radii of the surface), no stretching of the surface is involved by any changes in the principal radii of curvature which satisfy the condition  $R_1 R_2 = \text{constant}$ . In the neighbourhood of the vertex of the conic the resistance to bending makes both the principal radii of curvature finite, hence  $(R_1 R_2)^{-1}$  is finite (instead of zero as on the undistorted surfaces), and if  $s$  be any small area on the distorted surface, the amount of stretching due to the resistance to bending is  $(1 - \cos \theta)/(1 + \cos \theta)$ ,\* where  $\theta$  is the average angle which the edge of the distorted area makes with the original surface.

Where, as at AH, the generating lines cut the conic very obliquely, only one of the principal radii of curvature is appreciably affected, and the resistance to bending has hardly any effect in altering the area of the surface.

Thus absence of perfect flexibility causes a general rounding off of the sharp crease which forms the conic on the undistorted surface, a rounding off which is more and more marked as the distance from the vertex increases, and in addition to this, a knuckle-like prominence is produced in the neighbourhood of the vertex itself.

As a second example of simple folds, it may be seen at once that any rectangular plane surface can be folded without stretching into a series of cones such as are shown in photographs Nos. 8 and 9. In No. 9 the radius of curvature has the same sign in all the cones, but in No. 8 the curvature is alternately positive and negative. In both, when seen in plan, the average direction of the edges at right angles to the axes of the cones is parallel to direction of the corresponding edges of the plane before folding. When viewed in elevation, however (figs. 8A and 9A), it will be noticed that the free edges of the folds appear to be at right angles to the original plane in No. 8, where the curvature is alternately positive and negative, but at right angles to the slant side of the cones in No. 9.†

\* The stretching is not uniform over the area, but increases from 0 to a maximum at the boundary.

† It should be stated that the edges do not really lie in a plane, but the departure from a plane is of a very small order.

If, then, any number of equal rectangular sheets are folded as in fig. 8, they may be joined at the free edges of the folds without stretching and the average surface of the joined sheets will be a plane.

Sheets folded as in No. 9 may also have the free edges of their folds joined, but each sheet will now make an angle with the adjacent one equal to twice the angle which the slant side of the cones makes with the plane from which they were formed. Sheets thus joined are shown in the photograph (fig. 10) and in plan in fig. 10A.

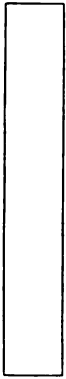


FIG. 8A.



FIG. 8.



FIG. 9.

FIG. 9A

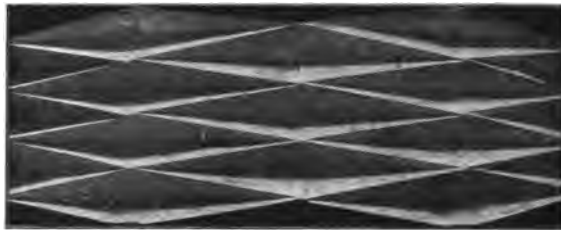


FIG. 10.

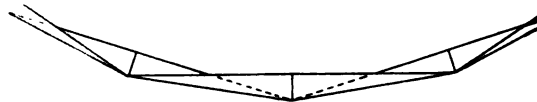


FIG. 10A.

Thus the cones of the combination of folded planes will all touch a cylinder, and the character of the surface of the combination will be analogous to, but not identical with, the intermediate stages of crushing of a tube by end pressure.

*Note on Horizontal Receivers and Transmitters in Wireless Telegraphy.*

By Prof. H. M. MACDONALD, F.R.S.

(Registered July 18, having been received by the Secretary at Cambridge,  
May 12,—Read November 19, 1908.)

In a communication published in the 'Proceedings,'\* Mr. Marconi has given the results observed when a straight horizontal conductor is substituted for the usual vertical conductor employed as a transmitter or receiver at a wireless telegraph station. The object of the following note is to consider the theory of such an arrangement, or at any rate one aspect of it. The receiver, as being the more important, will be considered first.

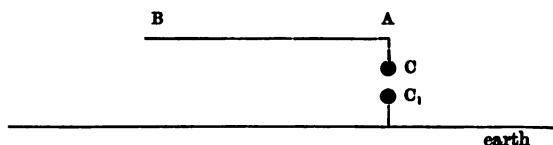


FIG. 1.

Let AB (fig. 1) represent the horizontal receiver, consisting of a straight conductor having the end A connected to a spark-gap CC<sub>1</sub> or other wave-detector. The electric oscillations in AB can be represented by a distribution of Hertzian oscillators along AB, and, if  $L$  denotes the current strength at any point of AB, it must satisfy the conditions  $L = 0$  at B, the free end, and  $dL/ds = 0$  at A, since the electric force perpendicular to AB at A must vanish. If the distance of AB from the earth is not too small, the effect of the oscillations belonging to the image in the earth of AB on those in AB may be neglected, the radiation from the free end B will be approximately symmetrical with respect to AB, and the oscillations in AB are then approximately the same as if BA formed part of a semi-infinite straight conductor in which a system of oscillations is being maintained, B being the free end and A the first node from the free end; the wave-length of these oscillations is very approximately five times the length of AB,† and therefore the receiver is of maximum efficiency when its length is one-fifth of the length of the transmitted wave, a result observed by Marconi.‡ When the distance of AB from the earth is so small that the effect of the oscillations in the image of AB in the earth on the oscillations in AB is not negligible, the radiation

\* Vol. 77, A, March, 1906.

† Macdonald, 'Electric Waves,' 1902, Ch. X.

‡ 'Roy. Soc. Proc., A, vol. 77, p. 421.

from the free end B will not be symmetrical with respect to AB, but may be taken as being approximately symmetrical with respect to some line through B making an angle with BA; the wave-length of the oscillations in AB is therefore equal to the wave-length of the oscillations in a bent conductor joining AB; that is greater than five times the length of AB, and, therefore, in this case the receiving conductor has its maximum efficiency when its length is somewhat less than one-fifth of the length of the transmitted wave, a result also observed by Marconi.\* To examine the effect of the orientation of the receiver, consider a straight conductor BAB' twice the length of AB (fig. 2) and its image  $B_1A_1B_1'$  in the horizontal plane, A and  $A_1$  being their middle points respectively.

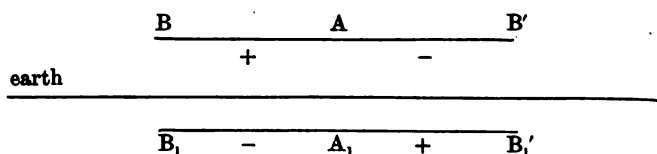


FIG. 2.

When electric oscillations are being maintained in BB' with the corresponding set in  $B_1B_1'$ , A and  $A_1$  are nodes, hence, if a wave-detector is placed in AA<sub>1</sub>, no effect will be observed in it due to its own oscillations, and therefore the potential difference at CC<sub>1</sub>, due to the forced oscillations in the receiver when the receiver AB is in the position fig. 1 is equal and opposite at any instant to the potential difference at CC<sub>1</sub> when the receiver is in the position which results from turning it through two right-angles round CC<sub>1</sub>. Now, the total effect at CC<sub>1</sub> is made up of two parts, one due to the direct action of the advancing waves, the other due to the oscillations in the receiver. If in fig. 1 the advancing waves be supposed to be travelling from left to right, the oscillations in the receiver may be regarded as the resultant of two sets of progressive waves, one travelling from B to A and the other from A to B; and, since the oscillations in the receiver are maintained by the advancing waves, the set of progressive waves in the receiver travelling from B to A must be in the same phase as the advancing waves at A. Further, since the electric force perpendicular to AB at A vanishes, the electric distribution on AC has at any instant the opposite sign to that on AB, and therefore the potential difference at CC<sub>1</sub> due to the oscillations in the receiver is at each instant in the opposite phase to the potential difference due to the direct action of the advancing waves. Hence, if  $\alpha$  denote the maximum potential difference at CC<sub>1</sub> due to the direct action of the advancing waves, and  $\beta$  the maximum potential difference due to the oscillations in the

\* *Loc. cit.*

receiver, the potential difference at  $CC_1$  at any instant is  $(\alpha - \beta) \cos pt$ . When AB is turned through two right-angles round  $CC_1$ , the advancing waves still travelling from left to right, the set of progressive waves in the receiver travelling from B to A must be in the opposite phase to the advancing waves at A, since the oscillations in the receiver are, as before, maintained by the advancing waves, and therefore the potential difference at  $CC_1$  due to the oscillations in the receiver is in this case in the same phase as that due to the direct action of the advancing waves, and is at any instant  $(\alpha + \beta) \cos pt$ . Hence the total effect at  $CC_1$  is greater when the free end B is pointing directly away from the transmitter than when it is pointing directly towards it. In the above the receiver AB has been assumed to be placed perpendicularly to the wave fronts of the advancing waves. When, in fig. 2,  $BB'$  is in the plane of the wave fronts of the advancing waves, no oscillations will be set up in  $BB'$ ; and, therefore, when  $BB'$  makes an angle  $\theta$  with the direction of the advancing waves, the amplitude of the oscillations in  $BB'$  lies between zero and the value corresponding to  $\theta = 0$ . Hence, when the receiver AB makes an angle  $\theta$  with the direction in which the transmitted waves are advancing, the potential difference at  $CC_1$  is  $\alpha \cos pt + f(\theta) \cos(pt + \epsilon)$ , where  $\beta > f(\theta) > 0$ , and  $\epsilon$  depends on  $\theta$ . If, then, a curve be drawn to represent the potential difference in terms of the orientation of the receiver, it will be of the form of the figure 8, with unequal loops, the larger loop being further from the transmitter, its greatest radius being  $\alpha + \beta$ .

When the horizontal conductor is used as a transmitter, its effect is made up of two sets of oscillations, one from the oscillations in the horizontal conductor emanating from the free end, the other from the vertical spark-gap. At a distance the effect of the first set is the same as that of a horizontal Hertzian oscillator with its image in the horizontal; hence, choosing axes of reference such that  $z$  is vertical and  $x$  is measured horizontally in the direction of AB, the vertical electric force at a distance due to this set is

$$B \frac{\partial^2}{\partial x \partial z} \cdot \frac{\partial}{\partial z} \frac{\sin \kappa (r - Vt)}{r}.$$

The vertical electric force due to the second set is

$$A \left( \frac{\partial^2}{\partial z^2} + \kappa^2 \right) \frac{\sin \kappa (r - Vt)}{r};$$

hence, retaining only the more important terms, the vertical electric force at the surface at a distance is

$$\left( A - B \frac{x}{r^2} \right) \frac{\kappa^2}{r} \sin \kappa (r - Vt) + A \frac{\kappa}{r^2} \cos \kappa (r - Vt),$$

where A and B have the same sign, as the waves proceeding from the free end are at the free end in approximately the opposite phase from those

proceeding from CC<sub>1</sub>. Hence the square of the amplitude of the vertical force at a distance is

$$\left(A - \frac{B}{r} \cos \theta\right)^2 \frac{\kappa^2}{r^2} + A^2 \frac{\kappa^2}{r^4},$$

where  $\theta$  is the angle the direction of the receiver makes with AB, and for a given value of  $r$  this gives a figure 8 curve, with unequal loops to represent the intensity of the transmitted waves.

[*Added August 31.*—The essential feature of the various systems of directed wireless telegraphy is the interference of two sets of waves differing in phase and proceeding from sources at a distance apart. Braun's\* arrangement consists of three vertical antennæ, each 20 metres high, placed at the corners of an equilateral triangle whose side is 30 metres. The waves proceeding from one of these differs in phase by  $\pi/2$  from the waves proceeding from the other two. For the best effect the perpendicular of the triangle is a quarter of a wave-length, as then the waves proceeding in one direction are in the same phase, while those proceeding in the opposite direction are in opposite phases. For this  $\lambda/4 = 30 \cos \pi/6$ , that is  $\lambda = 103$ , or approximately five times the height of the antenna, agreeing with theory.

Artom's† arrangement consists of two equal antennæ, each inclined at an angle of  $45^\circ$  to the horizontal, the oscillations in them differing in phase by  $\pi/2$ . The antennæ are bent through an angle of  $90^\circ$  at the ends above the horizontal, and led to conductors; the waves that interfere are those radiated from the bends, and the wave-length for the greatest effect will be greater than five times the length of the straight part of an antenna, the radiation from the bend not being symmetrical with respect to the antenna. For complete interference, that is, with the waves in one direction in the same phase, and the waves in the other direction in opposite phases, the distance between the two bends is a quarter of a wave-length; hence, if  $a$  is the length of the straight part of each of them,  $\lambda/4 = 2a \cos \pi/4$ , that is  $\lambda = 5.6a$ . In Marconi's‡ arrangement the two sources are the spark-gap and the free end of the horizontal conductor, whose distance apart is approximately one-fifth of a wave-length, while the oscillations differ in phase approximately  $\pi/2$ , the waves at the bend differing in phase by  $\pi$ . It should be observed that in Braun's arrangement and Artom's arrangement the amplitudes of the two component sets of waves are for all distances in the same constant ratio, while in Marconi's arrangement the amplitudes are in a ratio which varies as the distance.]

\* 'Jahrbuch Drahtl. Tele.,' vol. 1.

† 'Accad. dei Lincei,' Roma, vol. 15, p. 692, 1906.

‡ *Loc. cit.*



*The Propagation of Groups of Waves in Dispersive Media, with Application to Waves on Water produced by a Travelling Disturbance.*

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(Communicated by Prof. J. Larmor, Sec. R.S. Received August 26,—Read  
November 19, 1908.)

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§ 1. *Introduction.*

The object of this paper is to illustrate the main features of wave propagation in dispersive media. In the case of surface waves on deep water it has been remarked that the earlier investigators considered the more difficult problem of the propagation of an arbitrary initial disturbance as expressed by a Fourier integral, ignoring the simpler theory developed subsequently by considering the propagation of a single element of their integrals, namely, an unending train of simple harmonic waves. The point of view on which stress is laid here consists of a return to the Fourier integral, with the idea that the element of disturbance is not a simple harmonic wave-train, but a simple group, an aggregate of simple wave-trains clustering around a given central period. In many cases it is then possible to select from the integral

the few simple groups that are important, and hence to isolate the chief regular features, if any, in the phenomena.

In certain of the following sections well-known results appear; the aim has been to develop these from the present point of view, and so illustrate the dependence of the phenomena upon the character of the velocity function. In the other sections it is hoped that progress has been made in the theory of the propagation of an arbitrary initial group of waves, and also of the character of the wave pattern diverging from a point impulse travelling on the surface.

## § 2. *Definition of Simple Group.*

We have to consider the transmission of disturbances in a medium for which the velocity of propagation of homogeneous simple harmonic wave-trains is a definite function of the wave-length. The kinematically simplest group of waves is composed of only two simple trains, of wave-lengths  $\lambda, \lambda'$ , differing by an infinitesimal amount  $d\lambda$ ; then with the usual approximation we have for the combined effect

$$\begin{aligned} y &= A \cos \frac{2\pi}{\lambda} (x - Vt) + A \cos \frac{2\pi}{\lambda'} (x - V't) \\ &= 2A \cos \frac{\pi d\lambda}{\lambda^2} (x - Ut) \cos \frac{2\pi}{\lambda} (x - Vt), \end{aligned} \quad (1)$$

$$\text{where} \quad U = V - \lambda \frac{dV}{d\lambda}. \quad (2)$$

The expression (1) may be regarded as representing at any instant a train of wave-length  $\lambda$ , whose amplitude varies slowly with  $x$  according to the first cosine factor. Thus it does not represent a form which moves forward unchanged; but it has a certain periodic quality, for the form at any given instant is repeated after equal intervals of time  $\lambda/(V-U)$ , being displaced forward through equal distances  $\lambda U/(V-U)$ . The ratio of these quantities, namely  $U$ , is called the group-velocity. It has also the following significance: in the neighbourhood of an observer travelling with velocity  $U$  the disturbance continues to be approximately a train of simple harmonic waves of length  $\lambda$ .

The most general simple, or elementary, group may be defined in the following manner. Let the central form be a simple harmonic wave of length  $2\pi/\kappa_0$ , and let the other members be similar waves whose amplitude, wave-length, and velocity differ but slightly from the central type; then, with similar approximation, we have

$$\begin{aligned} y &= \Sigma A \cos \{ \kappa (x - Vt) + \alpha \} \\ &= \Sigma A_n \cos \{ \kappa_0 (x - V_0 t) + (x - U_0 t) \delta \kappa_n + \alpha \}. \end{aligned} \quad (3)$$

The range of values of  $\kappa$  being infinitesimal, the group as a whole may be written, as in the previous case, in the form

$$y = \phi(x - U_0 t) \cos \{\kappa_0(x - V_0 t) + \beta\}, \quad (4)$$

where  $\phi$  is a slowly varying function; and the group-velocity  $U_0$  is given by

$$U_0 = \frac{d}{d\kappa_0}(\kappa_0 V_0). \quad (5)$$

The group, to an observer travelling with velocity  $U_0$ , appears as consisting of approximately simple waves of length  $2\pi/\kappa_0$ . The simple group is, in fact, propagated as an approximately homogeneous simple wave-train; the importance of the group-velocity lies in the fact that any slight departure from homogeneity on a simple wave-train, due to local variation of amplitude or phase, is propagated with the velocity  $U$ .

### § 3. *The Fourier Integral regarded as a Collection of Groups.*

An arbitrary disturbance can, in general, be analysed by Fourier's method into a collection of simple wave-trains ranging over all possible values of  $\kappa$ ; thus after a time  $t$  the disturbance will be given by an expression of the type

$$\int_0^\infty \phi(\kappa) \cos \kappa(x - Vt + \alpha) d\kappa, \quad (6)$$

where  $V$  is a given function of  $\kappa$ .

The method adopted with these integrals is based on Lord Kelvin's\* treatment of the case, in which the amplitude factor  $\phi(\kappa)$  is a constant, so that

$$y = \int_0^\infty \cos \kappa(x - Vt) d\kappa.$$

An integral solution of this kind is constructed to represent the subsequent effect of an initial disturbance which is infinitely intense, and concentrated in a line through the origin; Lord Kelvin's process gives an approximate evaluation suitable for times and places such that  $x - Vt$  is large, and the argument may be stated in the following manner:—

In the dispersive medium the wave-trains included in each differential element of the varying period are mutually destructive, except when they are in the same phase and so cumulative for the time under consideration, this being when the argument of the undulation is stationary in value. Thus each differential element as regards period, in the Fourier integral, represents a disturbance which is very slight except around a certain point which itself changes with the time.

Now if we apply this method to the more general integral (6), we obtain an

\* Sir W. Thomson, 'Roy. Soc. Proc.' vol. 42, p. 80 (1887).

expression for the total disturbance, attending only to its prominent features and neglecting the rest, provided we assume the change of the amplitude factor  $\phi(\kappa)$  to be gradual. On this hypothesis the resulting expression contains the amplitude of the component trains simply as a factor; and in this way the trains for which it is a maximum show predominantly in the formula, which exhibits the main features of the disturbance as they arise from place to place through cumulation of synchronous component trains.

The argument shows that in some respects the integral (6) may be more conveniently regarded as a collection of travelling groups instead of simple wave-trains; when  $\phi(\kappa)$  is a slowly varying function, the groups will be simple groups of the type (3). The limitations within which this is the case will appear from the subsequent analysis; one method of procedure would be graphical: to take a graph of the fluctuating factor and see that the other factor, which is taken constant, does not vary much within the range that is important for the integral.

In the cases we shall examine, the effect is due to a limited initial disturbance, and the salient features are due to the circumstance that  $\phi(\kappa)$  has well-defined maxima; thus the prominent part of the effect can be expressed in the form of simple groups belonging to the neighbourhood of the maxima.

Before considering in detail special cases with assigned forms of the velocity function  $V$ , two illustrations of interest may be mentioned.

(a) *Damped harmonic wave-train.*—If  $f(x)$  is a function satisfying the conditions for the Fourier transformation, we have

$$f(x) = \frac{1}{\pi} \int_0^{\infty} d\kappa \int_{-\infty}^{\infty} f(\omega) \cos \kappa(\omega - x) d\omega.$$

For an even function of  $x$ , this gives

$$f(x) = \frac{2}{\pi} \int_0^{\infty} \phi(\kappa) \cos \kappa x d\kappa, \quad \text{where} \quad \phi(\kappa) = \int_0^{\infty} f(\omega) \cos \kappa \omega d\omega. \quad (7)$$

Now let  $f(x)$  be an even function of  $x$ , defined for all values, and such that it is equal to  $e^{-\mu x} \cos \kappa' x$  for  $x$  positive; then we find

$$2\phi(\kappa) = \frac{\mu}{\mu^2 + (\kappa - \kappa')^2} + \frac{\mu}{\mu^2 + (\kappa + \kappa')^2}. \quad (8)$$

Consider this function  $f(x)$  as the initial value of a disturbance  $y$  which occurs in a dispersive medium; then the value of  $y$  at any time can be expressed, in general, by

$$y = A \int_0^{\infty} \phi(\kappa) \cos \kappa(x - Vt) d\kappa + B \int_0^{\infty} \phi(\kappa) \cos \kappa(x + Vt) d\kappa, \quad (9)$$

where A, B are constants which need not be specified further in the present connection.

These integrals are of the type (6), and represent infinite wave-trains travelling in the positive and negative directions respectively. We see from (8) that when  $\mu$  is small, the amplitude factor  $\phi(\kappa)$  consists practically of a single well-defined peak in the neighbourhood of the value  $\kappa'$ . Hence, when the damping coefficient  $\mu$  is small, the wave-trains in question may be considered as travelling in the form of a group  $\kappa'$  of unchanging waves of this specified structure.

This example serves to illustrate the propagation of a very long train of simple harmonic waves subsiding as they travel owing to a small damping coefficient, and is of interest in connection with Lord Rayleigh's general proof that the group-velocity U is the velocity with which energy is being propagated.\* A small damping coefficient  $\mu$  is introduced by him, so that the energy transmitted is determined by the energy dissipated; the argument, which of course loses its meaning if  $\mu$  is actually zero, shows that when  $\mu$  is diminished indefinitely the rate of transmission of energy approaches U as a limiting value. Similarly, although the Fourier transformation is inapplicable when  $\mu$  is actually zero, we infer from the above analysis that when  $\mu$  is diminished indefinitely, the disturbance is representable as a simple group of unchanging waves of definite structure.

(b) *Interrupted simple wave-train.*—Consider an initial disturbance defined by

$$\begin{aligned} f(x) &= 0, & (-d < x < d) \\ &= e^{-\mu x} \sin \kappa' (x-d), & (x > d), \\ &= -e^{\mu x} \sin \kappa' (x+d), & (x < -d). \end{aligned}$$

Then the disturbance is given by an expression of the form (9), in which

$$\begin{aligned} 2\phi(\kappa) &= \int_{-d}^d e^{-\mu \omega} \cos \kappa' (\omega-d) \cos \kappa \omega d\omega \\ &= \frac{(\kappa + \kappa') \cos \kappa' d - \mu \sin \kappa' d}{\mu^2 + (\kappa + \kappa')^2} + \frac{(\kappa' - \kappa) \cos \kappa' d - \mu \sin \kappa' d}{\mu^2 + (\kappa' - \kappa)^2}. \end{aligned} \quad (10)$$

Now suppose  $\mu$  and  $d$  very small, so that the initial disturbance approximates to an infinite simple harmonic form with a narrow range of discontinuity; we see that the graph of the amplitude factor  $\phi(\kappa)$  is then reduced to a single peak in the vicinity of the value  $\kappa'$ . We infer from this example that a very long simple harmonic wave-train which is interrupted for a short interval is kinematically equivalent to a group of unchanging waves, of definite structure ranging round the value  $2\pi/\kappa'$  of the wavelength.

\* Lord Rayleigh, 'Proc. Lond. Math. Soc.,' vol. 9, p. 24 (1877).

§ 4. *Features of the Integrals Involved.*

The integrals we have to consider in such problems are of the type

$$y = \int \phi(u) \cos \{f(u)\} du. \quad (11)$$

All such integrals we can treat in the same manner, adopting the method employed by Lord Kelvin for the particular case referred to above (§ 3). This method consists in supposing that  $f(u)$  is large, so that the cosine factor is a rapidly varying quantity compared with the first factor; thus, much as in the Fresnel discussion of the diffraction of light waves, the prominent part of the graph of the integral is contained within a small range of  $u$  for which  $f(u)$  is stationary in value, so that the elements are then cumulative. In other words, we select from (11) the group or groups of terms ranging round values  $u_0$  of  $u$  which make

$$f'(u_0) = 0. \quad (12)$$

In such a group of terms we may put

$$f(u) = f(u_0) + \frac{1}{2}(u - u_0)^2 f''(u_0).$$

Then if we write  $\sigma^2$  for  $\frac{1}{2}(u - u_0)f''(u_0)$ , the contribution of the group to the value of (11) is given by

$$y_0 = \left\{ \frac{2}{f''(u_0)} \right\}^{\frac{1}{2}} \int_{-\infty}^{\infty} \phi(u_0) \cos \{f(u_0) + \sigma^2\} d\sigma, \quad (13)$$

where the limits of the integral may be in general extended, as in diffraction theory, to  $\pm \infty$ , provided  $u_0$  does not coincide with either limit of the integral (11), and also provided that  $f''(u_0)$  is not zero.

Thus we have, from (13),

$$\begin{aligned} y_0 &= \left\{ \frac{\pi}{f''(u_0)} \right\}^{\frac{1}{2}} \phi(u_0) [\cos \{f(u_0)\} - \sin \{f(u_0)\}] \\ &= \left\{ \frac{2\pi}{f''(u_0)} \right\}^{\frac{1}{2}} \phi(u_0) \cos \{f(u_0) + \frac{1}{4}\pi\}. \end{aligned} \quad (14)$$

This is the sum of the contributions of the constituents of each group around a central value  $u_0$  given by (12), provided the value  $u_0$  comes within the range of values of  $u$  in the integral (11).

If  $f''(u_0)$  is negative, the corresponding result may be written

$$y_0 = \left\{ \frac{2\pi}{-f''(u_0)} \right\}^{\frac{1}{2}} \phi(u_0) \cos \{f(u_0) - \frac{1}{4}\pi\}. \quad (15)$$

We write down for reference the similar pair of results for a group of terms from the integral

$$y = \int \phi(u) \sin \{f(u)\} du. \quad (16)$$

If  $f''(u_0)$  is positive,

$$y_0 = \left\{ \frac{2\pi}{f''(u_0)} \right\}^{\frac{1}{2}} \phi(u_0) \cos \{f(u_0) - \frac{1}{4}\pi\}; \quad (17)$$

and if  $f''(u_0)$  is negative,

$$y_0 = \left\{ \frac{2\pi}{-f''(u_0)} \right\}^{\frac{1}{2}} \phi(u_0) \cos \{f(u_0) + \frac{1}{4}\pi\}. \quad (18)$$

The chief form in which such integrals occur is

$$y = \int \phi(\kappa) \cos \kappa(x - Vt) d\kappa, \quad \text{where } V = f(\kappa). \quad (19)$$

The principal groups are given by the values  $\kappa_0$  such that

$$\frac{d}{d\kappa} \{\kappa(x - Vt)\} = 0, \quad \text{or} \quad \frac{x}{t} = \frac{d}{d\kappa} (\kappa V) = U. \quad (20)$$

The aggregate value of the group can be written down from one of the previous forms; if  $\partial U / \partial \kappa$  is negative, we should have

$$y_0 = \left\{ \frac{2\pi}{-t \partial U / \partial \kappa} \right\}^{\frac{1}{2}} \phi(\kappa_0) \cos \{\kappa_0(x - Vt) + \frac{1}{4}\pi\}. \quad (21)$$

As an illustrative example we may suppose a disturbance  $y$  to be given at time  $t$  by the expression\*

$$y = \int_0^\infty \cos \kappa(x - Vt) d\kappa. \quad (22)$$

When  $x - Vt$  is large, the elementary waves given by (22) reinforce each other only for the simple groups given by values  $\kappa_0$  for which the argument of the cosine is stationary, so that

$$x - Ut = 0. \quad (23)$$

This equation (23) defines a velocity  $U$  such that to an observer starting from the origin and travelling with this velocity the complex disturbance has the appearance of simple waves of length  $2\pi/\kappa_0$ . Or again, we may regard (23) as giving the predominant value of  $\kappa_0$  at any position and time in terms of  $x$  and  $t$ . The features of the disturbance will depend on the form of the velocity function  $V$ ; we proceed to consider some special forms.

### § 5. *Initial Line Displacement on Deep Water.*

We consider surface waves on an unlimited sheet of deep water, the only bodily forces being those due to gravity. Let the  $x$ -axis be in the undisturbed horizontal surface, and the  $y$ -axis be drawn vertically upwards. Let  $\eta$  be the elevation of surface waves of small amplitude with parallel crests and troughs perpendicular to the  $xy$ -plane. It can be shown that for an initial displace-

\* Lord Kelvin, *loc. cit. ante*.

ment given by  $\eta = \cos \kappa x$ , without initial velocity, the surface form at any subsequent time is given by

$$\eta = \cos \kappa Vt \cos \kappa x = \frac{1}{2} \{ \cos \kappa (x - Vt) + \cos \kappa (x + Vt) \},$$

where

$$V = (g/\kappa)^{\frac{1}{2}}. \quad (24)$$

Let  $f(x)$  be any even function of  $x$  which can be analysed by Fourier's integral theorem. Then, corresponding to an initial surface displacement  $f(x)$ , without initial velocity, there is a surface form given at any subsequent time by

$$\eta = \frac{1}{2\pi} \int_0^\infty \phi(\kappa) \cos \kappa (x - Vt) d\kappa + \frac{1}{2\pi} \int_0^\infty \phi(\kappa) \cos \kappa (x + Vt) d\kappa, \quad (25)$$

where

$$\phi(\kappa) = \int_{-\infty}^\infty f(\omega) \cos \kappa \omega d\omega. \quad (26)$$

If we suppose the initial elevation to be limited practically to a line through the origin and assume that  $\int_{-\infty}^\infty f(x) dx = 1$ , so that  $\phi(\kappa) = 1$ , we can use, as an illustration of the procedure, the form

$$\eta = \frac{1}{2\pi} \int_0^\infty \cos \kappa (x - Vt) d\kappa + \frac{1}{2\pi} \int_0^\infty \cos \kappa (x + Vt) d\kappa. \quad (27)$$

We select from these integrals the groups which give the chief regular features at large distances from the original disturbance. This cumulative group from the first integral is given for a given position and time by the value of  $\kappa$  for which  $\kappa (x - Vt)$  is stationary, where  $V = \sqrt{g/\kappa}$ , so that

$$\frac{x}{t} = U = \frac{1}{2} \sqrt{\frac{g}{\kappa}};$$

and, similarly, from the second integral by

$$-\frac{x}{t} = \frac{1}{2} \sqrt{\frac{g}{\kappa}}.$$

Thus there are symmetrical groups of waves proceeding in the two directions from the origin; for  $x$  positive we need only consider the first integral in (27), and for  $x$  negative the second integral. Thus the predominant wavelength at a point  $x$  at time  $t$  is given by

$$\kappa = gt^2/4x^2. \quad (28)$$

Evaluating this predominant group by means of expression (21), we obtain the known result

$$\eta = \frac{gt^{\frac{1}{2}}}{2\pi^{\frac{1}{2}}x^{\frac{1}{2}}} \cos \left( \frac{gt^2}{4x} - \frac{1}{2}\pi \right). \quad (29)$$

At a given position, far enough from the source for the train to be taken



as unlimited, this indicates oscillations succeeding each other with continually increasing frequency and amplitude; also if we follow a group of waves with given value of  $\kappa$  the amplitude varies inversely as  $t^{\frac{1}{2}}$ , or inversely as the square root of  $x$ .\*

### § 6. *Initial Displacement of Finite Breadth.*

If  $l$  is the range within which the initial displacement is sensible, the previous results hold with  $l/x$  small; further, as Cauchy showed,  $gt^2/4x^2$  must be small if the function  $\phi(\kappa)$  of (26) is to be taken as constant. Prof. Burnside† has obtained approximate equations for the surface form due to certain limited initial displacements not confined to an indefinitely narrow strip. From the present point of view, such results can be recovered simply by selecting from the integrals the more important groups of waves.

(a) Let the initial displacement be given by

$$f(x) = c\alpha^2/(\alpha^2 + x^2), \quad (30)$$

where  $\alpha$  may be supposed small.

Then 
$$\phi(\kappa) = \int_{-\infty}^{\infty} \frac{c\alpha^2 \cos \kappa \omega}{\alpha^2 + \omega^2} d\omega = \pi c\alpha e^{-\alpha\kappa}.$$

Hence from (25) the surface form is

$$\eta = \frac{1}{2}c\alpha \int_0^{\infty} e^{-\alpha\kappa} \cos \kappa(x - Vt) d\kappa + \frac{1}{2}c\alpha \int_0^{\infty} e^{-\alpha\kappa} \cos \kappa(x + Vt) d\kappa. \quad (31)$$

For points at some distance from the range in which the original disturbance was sensible,  $e^{-\alpha\kappa}$  varies slowly compared with the cosine term; thus we may consider the integrals as made up of simple groups. For  $x$  positive we need only consider the first integral.

The predominant value of  $\kappa$  is thus connected with  $x$  and  $t$  by the same equation (28) as before. Since the greater amplitudes are associated with the smaller values of  $\kappa$  and these have the greater values of  $U$ , it is clear that, at a particular point, the disturbance dies away from its maximum at a slower rate than its growth up to it. Using the previous results we can write down the disturbance involved in the main group form as

$$\eta = c\alpha\pi^{\frac{1}{2}} \frac{gt}{2x^{\frac{1}{2}}} e^{-\frac{gt^2}{4x^2}} \cos\left(\frac{gt^2}{4x} - \frac{1}{4}\pi\right). \quad (32)$$

The following results can be deduced. The cosine term varies rapidly compared with the other factors, hence we may obtain the maximum by considering the latter alone; it is easily seen that this occurs when

$$x/t = \sqrt{(\frac{1}{2}ga)}.$$

\* Lamb, 'Proc. Lond. Math. Soc.' (2), vol. 2, p. 371 (1904).

† W. Burnside, 'Proc. Lond. Math. Soc.', vol. 20, p. 22 (1888).

Thus the maximum is propagated out with uniform velocity; and we see that in its neighbourhood the predominant wave-length is  $4\pi\alpha$ .

(b) Let the initial displacement have a constant value  $A$  over a range of breadth  $2c$ , and be zero at all other points; then we have

$$\phi(\kappa) = 2A \frac{\sin \kappa c}{\kappa}.$$

Hence the surface elevation is

$$\eta = \frac{A}{\pi} \int_0^\infty \frac{\sin \kappa c}{\kappa} \cos \kappa (x - Vt) d\kappa + \frac{A}{\pi} \int_0^\infty \frac{\sin \kappa c}{\kappa} \cos \kappa (x + Vt) d\kappa. \quad (33)$$

With the same argument as before, we consider the value of  $\eta$  at a point as due to the most important of a succession of simple groups, that one, namely, for which the argument is there stationary so that the components reinforce over a considerable range of  $\kappa$ ; and we can write down, from the previous results, an expression for this group which is valid at least in the vicinity of the travelling maxima of the disturbance. We have

$$\eta = \frac{4A}{\pi^{\frac{1}{2}}} \left( \frac{x}{gt^2} \right)^{\frac{1}{2}} \sin \frac{gt^2 c}{4x^2} \cos \left( \frac{gt^2}{4x} - \frac{1}{2}\pi \right), \quad (34)$$

corresponding to Burnside's result in the paper already cited.

Here we have a succession of maxima given by those of  $(x/gt^2)^{\frac{1}{2}} \sin(gt^2/4x^2)$ , that is, at times given by  $\tan \theta = 2\theta$ , where  $\theta = gt^2/4x^2$ .

The period of the group that is thus cumulative is different for different localities, and for different times at the same locality; but the accumulation is very prominent only for those times and localities which give a maximum value to the amplitude, which has been graphed for the next example in fig. 1.

The maxima here diminish continually in value, and are propagated each with uniform velocity, namely, the group-velocity corresponding to the predominant wave-length in the neighbourhood.

### § 7. *Limited Train of Simple Oscillations.*

Another interesting example is the case of an initial displacement consisting of a limited length of simple harmonic oscillations. If  $f(x)$  is symmetrical with respect to the origin, and is zero except for a range of  $(2n + \frac{1}{2})$  wave-lengths within which it is  $A \cos \kappa'x$ , we have

$$\phi(\kappa) = 2 \int_0^{(2n+\frac{1}{2})\pi/\kappa'} A \cos \kappa' \omega \cos \kappa \omega d\omega = 2\kappa' A \frac{\cos(2n+\frac{1}{2})\pi\kappa/\kappa'}{\kappa'^2 - \kappa^2}. \quad (35)$$

Hence, from (25), we have the surface elevation  $\eta$ , of which we write down

only the integral necessary for propagation in the direction of  $x$  positive, that is,

$$\eta = \frac{\kappa' A}{\pi} \int_0^\infty \frac{\cos(2n + \frac{1}{2}) \pi \kappa / \kappa'}{\kappa'^2 - \kappa^2} \cos \kappa (x - Vt) d\kappa. \quad (36)$$

If  $n$  is very large, the main feature consists of the component waves round the value  $\kappa'$ ; but in general it is to be noticed that a series of subsidiary components appears whose effects may be of sufficient magnitude to be appreciable. But the component waves are cumulative only for values of  $x$  and  $t$  such that

$$\kappa = gt^2/4x^2,$$

which is the value corresponding to a stationary argument of the cosine; thus the prominent effect at time  $t$ , of any group of parameter  $\kappa$ , will be at localities where  $\kappa$  has the value  $\kappa'$ , or, else, a value belonging to one of the subsidiary maxima. The result may be evaluated in the same manner as before; we find

$$\eta = 16\kappa' A \left(\frac{g}{\pi}\right)^{\frac{1}{2}} \frac{x^{\frac{1}{2}} t}{16\kappa'^2 x^4 - g^2 t^4} \cos(2n + \frac{1}{2}) \frac{\pi g t^2}{4\kappa' x^2} \cos\left(\frac{g t^2}{4x} - \frac{1}{4}\pi\right). \quad (37)$$

We can obtain the prominent travelling groups above referred to, which this involves, by evaluating the maxima of the amplitude function

$$\frac{t}{16\kappa'^2 x^4 - g^2 t^4} \cos(2n + \frac{1}{2}) \frac{\pi g t^2}{4\kappa' x^2}. \quad (38)$$

The form of this function is shown by fig. 1; it is obtained by plotting the curve

$$y = \frac{\alpha}{1 - \alpha^4} \cos \frac{3}{2} \pi \alpha^2, \quad (39)$$

where  $\alpha$  is proportional to  $t$ , and, further,  $\alpha$  equal to 1 corresponds to  $\kappa$  equal to  $\kappa'$ .

The curve represents the variation of the disturbance at a given point with the time, neglecting the local variations of the last cosine factor in (37); it shows the grouped propagation of an initial displacement consisting of  $4\frac{1}{2}$  complete wave-lengths of a simple cosine wave of wave-length  $2\pi/\kappa'$ , or  $\lambda'$ .

The main undulatory disturbance appears as a simple group around the predominant wave-length  $\lambda'$ , moving forward with the corresponding group-velocity  $\frac{1}{2}\sqrt{(g/\kappa')}$  or  $\frac{1}{2}V$ . But *in advance* of this main group of undulations there are two or three subsidiary groups of sensible magnitude with wave-lengths in the neighbourhood of  $9\lambda/2$ ,  $9\lambda/4$ ,  $9\lambda/6$ , moving with corresponding group-velocities of  $3V/2\sqrt{2}$ ,  $3V/4$ ,  $3V/2\sqrt{6}$ . Thus in advance of the main group we have slighter groups of larger wave-lengths moving with group-velocities which may be larger than the wave-velocity of the original dis-

turbance if it were unlimited. In the *rear* of the main group we have also a series of alternating groups, following each other much more quickly and with their wave-lengths and velocities less separated out than in the front of the main group. Hence the disturbance in the rear, especially at distances from the origin not very great, may be expected to consist of small, more

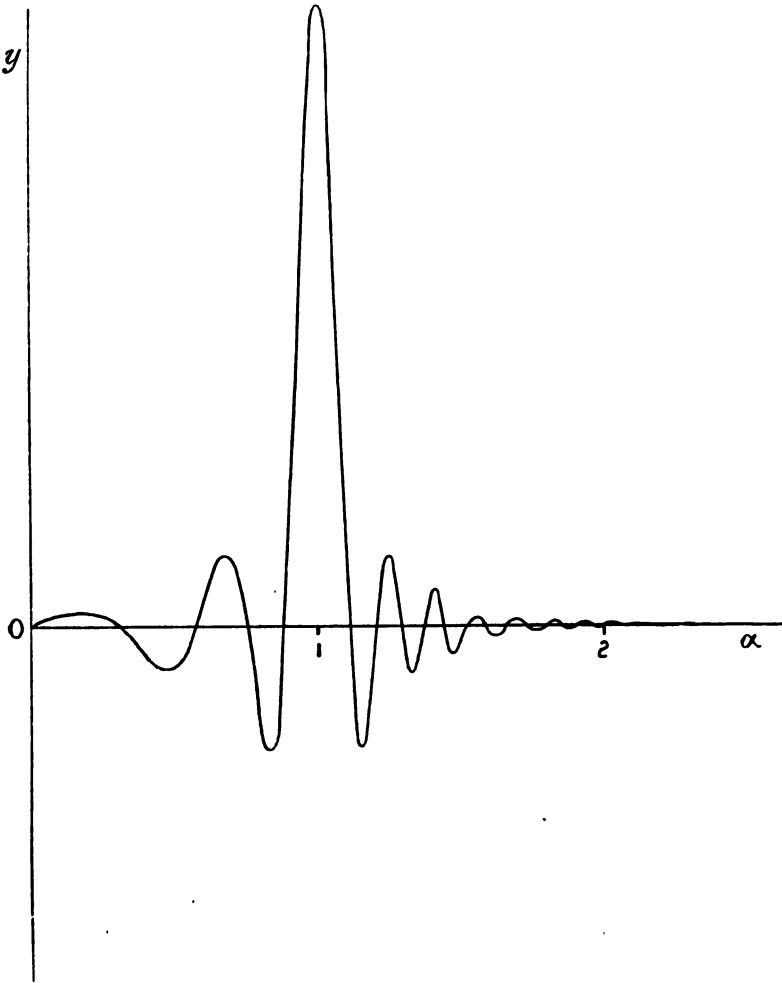


FIG. 1.

irregular, motion resulting from the superposition of this latter system of groups, thus there will be a more distinctive rear of disturbance moving forward with velocity  $\frac{1}{2}V$ . These inferences may be compared with some results given in Lord Kelvin's later papers. Starting from a solution of the equations for an initial elevation in the form of a single crest, the results were combined graphically so as to show in a series of figures the propagation of

an initial disturbance consisting of five crests and four hollows of approximately sinusoidal shape; the following remarks are made:—\* “Immediately after the water is left free, the disturbance begins analysing itself into two groups of waves, seen travelling in contrary directions from the middle line of the diagram. The perceptible fronts of these two groups extend rightwards and leftwards from the end of the initial static group far beyond the ‘hypothetical fronts,’ supposed to travel at half the wave-velocity, which (according to the dynamics of Osborne Reynolds and Rayleigh, in their important and interesting consideration of the work required to feed a uniform procession of water-waves) would be the actual fronts *if* the free groups remained uniform. How far this *if* is from being realised is illustrated by the diagrams of fig. 35, which show a great extension outwards in each direction far beyond distances travelled at half the ‘wave-velocity.’ While there is this great extension of the fronts outward from the middle, we see that the two groups, after emergence from coexistence in the middle, travel with their rears leaving a widening space between them of water not perceptibly disturbed, but with very minute wavelets in ever augmenting number following slower and slower in the rear of each group. The extreme perceptible rear travels at a speed closely corresponding to the ‘half wave-velocity.’ . . . . Thus the perceptible front travels at speed actually higher than the wave-velocity, and this perceptible front becomes more and more important relatively to the whole group with the advance of time . . . .”

This extract will serve to emphasise the importance of strict definition and use of the word “group.” A simple group, of whatever structure, has associated with it a definite velocity depending only on the wave-length, but not so an arbitrary limited displacement. In various cases we have found it convenient to analyse such into its important elementary groups, each with definite velocity; in special cases the disturbance may be equivalent practically to one simple group.

#### § 8. *Initial Impulse on Deep Water.*

Suppose that initially the surface is horizontal, but that given impulses are applied to it. Then for any given symmetrical distribution of impulse  $f(x)$ , suitable for Fourier analysis, with no initial elevation, the surface elevation at any subsequent time is given by

$$\pi g p \eta = \frac{1}{2} \int_0^{\infty} \kappa V \phi(\kappa) \sin \kappa(x - Vt) d\kappa - \frac{1}{2} \int_0^{\infty} \kappa V \phi(\kappa) \sin \kappa(x + Vt) d\kappa, \quad (40)$$

where

$$\phi(\kappa) = \int_{-\infty}^{\infty} f(\omega) \cos \kappa \omega d\omega.$$

\* Lord Kelvin, ‘Phil. Mag.’ vol. 13, p. 11 (1907).

If we assume  $\phi(\kappa)$  equal to 1, so that it is confined to an indefinitely narrow strip of impulse (cf. § 5), we obtain the result corresponding to (29) for initial displacement by multiplying that expression by the value of  $\kappa V$ ; thus we find

$$\eta = \frac{gt^2}{4\pi^{\frac{1}{2}}\rho x^{\frac{1}{2}}} \cos\left(\frac{gt^2}{4x} + \frac{1}{4}\pi\right). \quad (41)$$

For comparison with the previous results, suppose that

$$f(x) = \frac{c\alpha^2}{\alpha^2 + x^2}, \quad \phi(\kappa) = \pi c\alpha e^{-\alpha\kappa}.$$

Then we find the surface form as an aggregate of groups, each of them cumulative and so prominent only in a limited region, given by

$$\eta = \frac{\pi^{\frac{1}{2}}cag^{\frac{1}{2}}t^2}{4\rho x^{\frac{1}{2}}} e^{-\frac{a}{4x^2}} \cos\left(\frac{gt^2}{4x} + \frac{1}{4}\pi\right). \quad (42)$$

For a given place the maxima are given by

$$\frac{d}{dt}(t^2 e^{-ga^2/4x^2}) = 0, \quad \text{that is, by} \quad \frac{x}{t} = \frac{1}{2}\sqrt{ga}.$$

Thus the maximum moves with velocity  $\frac{1}{2}\sqrt{ga}$ , and consists of nearly simple waves of wave-length  $2\pi\alpha$ . Comparing with the result in § 6 for an initial displacement of the same character, we see that the maximum is propagated outwards with slower velocity, the wave-length at the maximum being one-half the corresponding value in the former case.

### § 9. *Moving Line Impulse on Deep Water.*

Suppose that the line impulse of the previous section is moving over the surface of deep water at right angles to its length with uniform velocity  $c$ , having started at some time practically infinitely remote. Then we may regard the effect at  $(x, t)$  as the summation of the effects due to all the consecutive elements of impulse, and we can obtain an expression by modifying (40) and integrating with respect to the time. We measure  $x$  from a fixed origin which the line impulse passes at zero time; then we substitute  $x - ct_0$  for  $x$  and  $t - t_0$  for  $t$  in (40), and integrate with respect to  $t_0$  for all the time the impulse has been moving. Thus we obtain

$$\begin{aligned} \pi g \rho \eta &= \frac{1}{2} \int_{-\infty}^t dt_0 \int_0^{\infty} \kappa V \sin \kappa \{x - ct_0 - V(t - t_0)\} d\kappa \\ &\quad - \frac{1}{2} \int_{-\infty}^t dt_0 \int_0^{\infty} \kappa V \sin \kappa \{x - ct_0 + V(t - t_0)\} d\kappa \\ &= \frac{1}{2} \int_0^{\infty} du \int_0^{\infty} \kappa V \sin \kappa \{\varpi + (c - V)u\} d\kappa \\ &\quad - \frac{1}{2} \int_0^{\infty} du \int_0^{\infty} \kappa V \sin \kappa \{\varpi + (c + V)u\} d\kappa, \quad (43) \end{aligned}$$

where  $\varpi = x - ct$ , and represents distance in advance of the present position of the impulse. We proceed to obtain now the important regular features of the disturbance represented by these integrals.

With the notation of (19) and (20) we have in the first integral

$$f(\kappa) = c - V = c - \sqrt{g/\kappa},$$

$$\frac{d}{d\kappa} \{ \kappa f(\kappa) \} = c - \frac{1}{2} \sqrt{g/\kappa}.$$

Hence the required predominant value of  $\kappa$ , which corresponds to a stationary argument, is given by

$$c - \frac{1}{2} \sqrt{\frac{g}{\kappa}} = -\frac{\varpi}{u}, \quad \text{or} \quad \kappa = \frac{gu^2}{4(cu + \varpi)^2}. \quad (44)$$

Thus the first integral in (43) gives

$$\frac{1}{4} \pi^{\frac{1}{2}} g^{\frac{1}{2}} \int_0^{\infty} \frac{u^2}{(\varpi + cu)^{\frac{1}{2}}} \cos \left\{ \frac{gu^2}{4(\varpi + cu)} + \frac{1}{4} \pi \right\} du. \quad (45)$$

We choose again the principal groups of oscillations by the condition

$$\frac{d}{du} \left\{ \frac{gu^2}{4(\varpi + cu)} + \frac{1}{4} \pi \right\} = 0, \quad \text{or} \quad cu = -2\varpi.$$

Now  $u$  must be positive to come within the range of the integral (45); hence if  $\varpi$  is positive we obtain no contribution towards a regular undulatory disturbance. If  $\varpi$  is negative we obtain a series of travelling waves which we can evaluate from (45).

We have

$$\frac{d^2}{du^2} \left\{ \frac{gu^2}{4(\varpi + cu)} + \frac{1}{4} \pi \right\} = -\frac{g}{2\varpi}, \quad \text{when} \quad cu = -2\varpi.$$

Hence, using expression (18), we obtain the value of the chief group from (45), namely,

$$\frac{2\pi g}{c^2} \sin \frac{g\varpi}{c^2}, \quad (46)$$

which holds when  $\varpi$  is negative.

As regards the second integral in (43), we easily see by taking the principal group in  $\kappa$  that  $\varpi + cu$  must be negative: thus  $\varpi$  must be negative and  $cu$  between zero and  $\varpi$  numerically. Then taking the chief group in  $u$ , we have  $cu$  equal to  $2\varpi$  numerically. Hence there is no resulting group of waves falling in the range, and the second integral contributes nothing to the regular disturbance.

We have then the well-known result that in front of the travelling impulse there is no regular disturbance, while in the rear there is a train of regular waves, proportional to (46), with wave-length suitable to the velocity  $c$ .

The same method can be used for waves on water of depth  $h$ , due to a travelling impulse system. For in the integrals (43) we should have

$$f(\kappa) = c - V = c - \sqrt{\left(\frac{g}{\kappa} \tanh \kappa h\right)}. \quad (47)$$

The group with respect to  $\kappa$  would give a term proportional to

$$\cos \{u\kappa^2 f'(\kappa) + \frac{1}{4}\pi\}, \quad (48)$$

where  $\kappa$  has the value given by

$$-u/u = f(\kappa) + \kappa f'(\kappa). \quad (49)$$

We then select the group with respect to  $u$  by

$$\frac{d}{du} \{u\kappa^2 f'(\kappa)\} = 0. \quad (50)$$

Using (49) we find this leads to\*

$$f(\kappa) = 0, \quad \text{or} \quad V = c = \sqrt{(gh)} \sqrt{\left(\frac{\tanh \kappa h}{\kappa h}\right)}. \quad (51)$$

Since  $\tanh \kappa h / \kappa h$  diminishes continually from 1 to 0 as  $\kappa h$  increases from 0 to  $\infty$ , there is only a real solution of (51) when  $c^2$  is less than  $gh$ . In this case we have regular waves of length suitable to velocity  $c$  following in the rear of the impulse; when  $c$  is greater than the maximum wave-velocity there is no regular wave form.

#### § 10. *Capillary Surface Waves.*

In order to illustrate the propagation of an element of the Fourier expression as a limited travelling group of undulations, we consider another form of velocity function. If waves are propagated over the surface of a liquid of density  $\rho$  under the action of the surface tension  $T$ , it can be shown that the velocity of simple waves of length  $2\pi/\kappa$  is

$$V = \sqrt{(T\kappa/\rho)}. \quad (52)$$

Hence in this case the group-velocity is

$$U = \frac{3}{2}\sqrt{(T\kappa/\rho)} = \frac{3}{2}V;$$

thus the group-velocity is greater than the wave-velocity, and we shall see how this affects some of the previous results.

(a) *Initial elevation consisting of  $(2n + \frac{1}{2})$  simple oscillations of wave-length  $2\pi/\kappa'$ .*—If we consider the same problem as in § 7 we have

$$\eta = A \int_0^\infty \frac{\cos(2n + \frac{1}{2})\pi\kappa/\kappa'}{\kappa'^2 - \kappa^2} \cos \kappa(x - Vt) d\kappa. \quad (53)$$

\* Cf. Lord Rayleigh, 'Phil. Mag.,' vol. 10, p. 407 (1905).



The predominant value of  $\kappa$ , for given time and place, is given by

$$\kappa = 4\rho x^2/9Tt^2. \quad (54)$$

The chief groups, each with approximately constant amplitude, are given by

$$\eta = A' \frac{x^{\frac{1}{2}} t^3}{81T^2 \kappa'^2 t^4 - 16\rho^2 x^4} \cos(2n + \frac{1}{2}) \frac{4\pi\rho x^2}{9\kappa' T t^2} \cos\left(\frac{4\rho x^3}{27T t^3} - \frac{1}{4}\pi\right). \quad (55)$$

At a given place the maxima of amplitude are those of

$$\frac{t^3}{81T^2 \kappa'^2 t^4 - 16\rho^2 x^4} \cos(2n + \frac{1}{2}) \frac{4\pi\rho x^2}{9\kappa' T t^2}. \quad (56)$$

Fig. 2 represents the curve

$$y = \frac{\alpha^3}{\alpha^4 - 1} \cos \frac{9\pi}{2\alpha^2}, \quad (57)$$

where  $\alpha$  is proportional to the time and  $\alpha$  equal to 1 corresponds to  $\kappa$  equal to  $\kappa'$ .

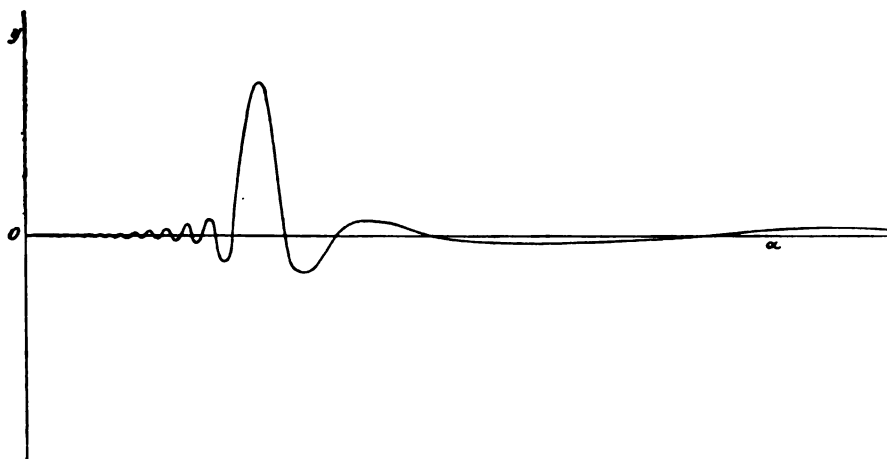


FIG. 2.

Comparing this with § 7 we draw the inference that in this case the perceptible front of the advancing train is more clearly marked than the rear and advances with the half-wave-velocity corresponding to  $\kappa'$ , in agreement with simple observation.

(b) *Moving line impulse.*—A line impulse at rest leads to

$$\eta = Cx^{\frac{1}{2}} t^{-4} \cos\left(\frac{4\rho x^3}{27T t^3} + \frac{1}{4}\pi\right).$$

Consequently a moving line impulse will give

$$\eta = A \int_0^\infty \frac{(\varpi + cu)^{\frac{1}{2}}}{u^4} \cos\left\{\frac{4\rho}{27T} \frac{(\varpi + cu)^3}{u^3} + \frac{1}{4}\pi\right\} du. \quad (58)$$

Then we choose  $u$  so that

$$\frac{d}{du} \left\{ \frac{(\varpi + cu)^3}{u^3} \right\} = 0, \quad \text{or} \quad u(cu - 2\varpi)(\varpi + cu)^2 = 0.$$

The value giving a regular wave pattern is the positive root

$$cu = 2\varpi, \quad \text{for } \varpi \text{ positive.}$$

Hence in this case we have a regular train of waves of length suitable to the velocity  $c$  in *advance* of the moving pressure system, with no regular pattern in the rear.

### § 11. *Water Waves due to Gravity and Capillarity.*

If we take account of gravity and the surface tension together, we have the velocity function

$$V = (T\kappa + g/\kappa)^{\frac{1}{2}}. \quad (59)$$

Hence

$$U = \frac{d}{d\kappa} (\kappa V) = \frac{3T\kappa^2 + g}{2(T\kappa^3 + g\kappa)^{\frac{1}{2}}}. \quad (60)$$

We have not here a simple ratio  $U/V$ , independent of  $\kappa$ . The velocity  $V$  has a minimum  $c_m$  for a certain value  $\kappa_m$ , equal to  $(g/T)^{\frac{1}{3}}$ , and for this value  $U$  is equal to  $V$ —as in fact follows from the definition of  $U$ . For  $\kappa < \kappa_m$ ,  $U$  is less than  $V$ , tending ultimately to  $\frac{1}{2}V$ ; while for  $\kappa > \kappa_m$ ,  $U$  is greater than  $V$  and approaches as a limit  $\frac{3}{2}V$ .

If we consider a travelling line impulse, the whole problem of finding the principal groups is contained in the equations

$$\left. \begin{aligned} \frac{\varpi + cu}{u} = U &= \frac{3T\kappa^2 + g}{2(T\kappa^3 + g\kappa)^{\frac{1}{2}}} \\ c = V &= (T\kappa + g/\kappa)^{\frac{1}{2}} \end{aligned} \right\}. \quad (61)$$

$$\text{Hence} \quad c^2 u^2 = \frac{4c^4 \varpi^2}{c^4 - c_m^4}, \quad \kappa = \frac{c^2 \pm (c^4 - c_m^4)^{\frac{1}{2}}}{2T},$$

where the positive sign is taken for  $\varpi$  positive (in advance of the impulse), and the negative sign for  $\varpi$  negative (in the rear). Thus there is no wave pattern unless  $c$  is greater than the minimum wave-velocity  $c_m$ ; and if so there are regular trains both in advance and in the rear, the smaller wave-lengths being in advance. With the ratio  $c/c_m$  large, the results approximate to very small waves in front and waves in the rear with  $\kappa$  equal to  $g/c^2$ .

### § 12. *Surface Waves in two Dimensions.*

Suppose that the initial data instead of being symmetrical about a transverse straight line are symmetrical around the origin. Let the axes of

$x, y$  be in the undisturbed surface and the axis of  $z$  vertically upwards; we write  $\varpi$  for  $\sqrt{(x^2 + y^2)}$ . Then, corresponding to (25), the surface elevation  $\zeta$  due to an initial displacement  $f(\varpi)$ , set free without initial velocity, is given by

$$\zeta = \int_0^\infty J_0(\kappa\varpi) \cos(\kappa Vt) \phi(\kappa) \kappa d\kappa, \quad (62)$$

where

$$\phi(\kappa) = \int_0^\infty f(\alpha) J_0(\kappa\alpha) \alpha d\alpha. \quad (63)$$

For an initial point-elevation we may take for simplicity  $\phi(\kappa)$  equal to  $1/2\pi$ ; then we have

$$\begin{aligned} \zeta &= \frac{1}{2\pi} \int_0^\infty J_0(\kappa\varpi) \cos(\kappa Vt) \kappa d\kappa \\ &= \frac{1}{\pi^2} \int_0^{\pi/2} d\beta \int_0^\infty \cos(\kappa\varpi \cos \beta) \cos(\kappa Vt) \kappa d\kappa \\ &= \frac{1}{2\pi^2} \int_0^{\pi/2} d\beta \int_0^\infty \cos \kappa (\varpi \cos \beta - Vt) \kappa d\kappa \\ &\quad + \frac{1}{2\pi^2} \int_0^{\pi/2} d\beta \int_0^\infty \cos \kappa (\varpi \cos \beta + Vt) \kappa d\kappa. \end{aligned} \quad (64)$$

For deep water we separate a real principal group from the first integral, with respect to  $\kappa$ , around the value of  $\kappa$  given by

$$\frac{\varpi \cos \beta}{t} = \frac{1}{2} \sqrt{\frac{g}{\kappa}}.$$

This is replaced by the equivalent form

$$\zeta = \frac{g^{1/2} t^3}{8\pi^{1/2} \varpi^3} \int_0^{\pi/2} \frac{d\beta}{\cos^3 \beta} \cos \left( \frac{gt^2}{4\varpi \cos \beta} - \frac{1}{2}\pi \right). \quad (65)$$

Considering now the range for  $\beta$ , we can again select the principal group of oscillations from (65); it occurs at  $\beta$  equal to zero, so we take one-half the result given by the expression (14) and obtain the known result

$$\zeta = \frac{gt^2}{2^{1/2} \pi \varpi^3} \cos \frac{gt^2}{4\varpi}. \quad (66)$$

Similarly, for an initial point impulse we have, instead of (64), the expression

$$\zeta = \frac{1}{2g\rho\pi^2} \int_0^{\pi/2} d\beta \int_0^\infty \kappa V \{ \sin \kappa (\varpi \cos \beta - Vt) - \sin \kappa (\varpi \cos \beta + Vt) \} \kappa d\kappa, \quad (67)$$

leading in the same way to the result

$$\zeta = -\frac{gt^3}{2^{1/2} \pi \rho \varpi^4} \sin \frac{gt^2}{4\varpi}. \quad (68)$$

§ 13. *Point Impulse Travelling over Deep Water.*

Let the impulse be moving along  $Ox$  with constant velocity  $c$ ; let  $B$  be the position at time  $t$ ,  $A$  at any previous time  $t_0$ , and suppose the system to have been moving for an indefinitely long time.

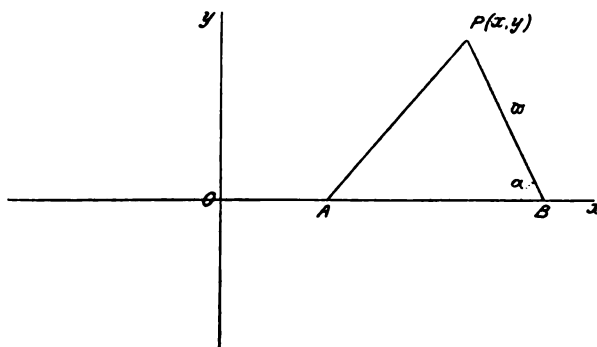


FIG. 3.

We have

$$OA = ct_0; \quad OB = ct;$$

$$PB = \varpi = \{(ct-x)^2 + y^2\}^{\frac{1}{2}};$$

$$\cos \alpha = (ct-x)/\varpi.$$

Then in (67) we have to substitute  $\{\varpi^2 - 2c(t-t_0)\cos \alpha + c^2(t-t_0)^2\}^{\frac{1}{2}}$  for  $\varpi$ ,  $t-t_0$  for  $t$ , and integrate with respect to  $t_0$  from  $-\infty$  to  $t$ ; we obtain

$$\zeta = \frac{1}{2g\rho\pi^2} \int_0^{\pi/2} d\beta \int_0^\infty du \int_0^\infty \kappa V [\sin \kappa (\cos \beta \{\varpi^2 - 2cu\cos \alpha + c^2u^2\}^{\frac{1}{2}} - Vu) \\ - \sin \kappa (\cos \beta \{\varpi^2 - 2cu\cos \alpha + c^2u^2\}^{\frac{1}{2}} + Vu)] \kappa d\kappa. \quad (69)$$

With  $V = (g/\kappa)^{\frac{1}{2}}$ , we select the group around the value of  $\kappa$  given by

$$\kappa^{-1} = 4 \cos^2 \beta (\varpi^2 - 2cu\cos \alpha + c^2u^2)/gu^2. \quad (70)$$

By using the formula (17) we find

$$\zeta = \frac{g^{\frac{1}{2}}}{16\rho\pi^{\frac{1}{2}}} \int_0^\infty du \int_0^{\pi/2} \frac{u^4 d\beta}{\cos^{\frac{1}{2}} \beta (\varpi^2 - 2cu\cos \alpha + c^2u^2)^{\frac{1}{2}}} \\ \cos \left\{ \frac{gu^2}{4 \cos \beta (\varpi^2 - 2cu\cos \alpha + c^2u^2)^{\frac{1}{2}}} + \frac{1}{4}\pi \right\}. \quad (71)$$

Selecting from this the chief group which occurs near  $\beta$  equal to zero, we find

$$\zeta = -\frac{g}{2^{\frac{1}{2}}\pi\rho} \int_0^\infty \frac{u^3 du}{(\varpi^2 - 2cu\cos \alpha + c^2u^2)^{\frac{3}{2}}} \sin \frac{gu^2}{4(\varpi^2 - 2cu\cos \alpha + c^2u^2)^{\frac{1}{2}}}. \quad (72)$$

Finally we choose the chief groups of terms in  $u$  from the condition

$$\frac{d}{du} \frac{1}{4} gu^2 (\varpi^2 - 2cu\cos \alpha + c^2u^2)^{-\frac{1}{2}} = 0; \quad (73)$$

that is, from 
$$c^2u^2 - 3cu\pi \cos \alpha + 2\pi^2 = 0, \quad (74)$$

or 
$$cu = \frac{1}{2}\pi \{3 \cos \alpha \pm (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}, \quad (75)$$

We have then different cases to consider according to the nature of these values for  $cu$ , remembering that  $cu$  gives a position of the moving impulse, at time  $u$  previously, for which the waves sent out reinforce each other at the point  $(\pi, \alpha)$  at time  $t$ .

(i) In the region where  $9 \cos^2 \alpha < 8$ , both roots are imaginary; thus the previous position is non-existent, and there is no principal group in the integral (72). Hence all the regular wave pattern is contained within two straight lines radiating from the point impulse, each making with the line of motion an angle  $\cos^{-1} 2\sqrt{2}/3$ , or approximately  $19^\circ 28'$ .

(ii) When  $9 \cos^2 \alpha > 8$ , there are two different real roots for  $cu$ . Thus we have two chief groups in the integral (72), corresponding to two regular wave systems superposed on each other.

At any point P within the two bounding radii the disturbance consists of two parts: one part sent out from A at time  $u_1$  previously, where

$$OA = \frac{1}{2}\pi \{3 \cos \alpha + (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\} \text{ and } u_1 = OA/c; \quad (76)$$

and another part sent out from B at time  $u_2$  before, where

$$OB = \frac{1}{2}\pi \{3 \cos \alpha - (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\} \text{ and } u_2 = OB/c. \quad (77)$$

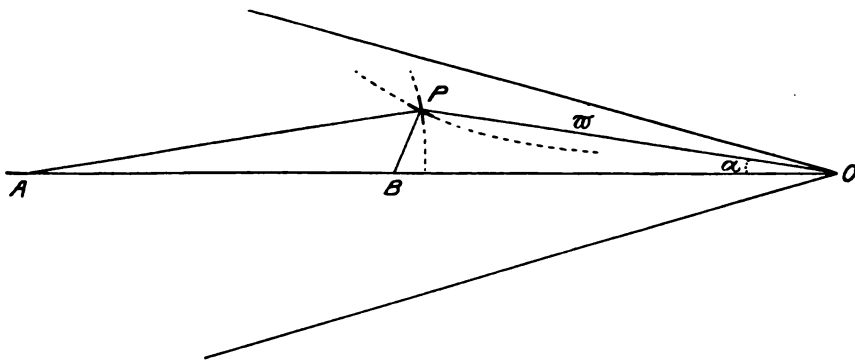


FIG. 4.

We have then two wave systems, which may be called the transverse waves and the diverging waves; we shall examine them separately.

(a) *The transverse wave system.*—Taking the larger value of  $cu$  in (76) we find

$$\begin{aligned} \pi^2 - 2cu\pi \cos \alpha + c^2u^2 &= \frac{1}{4}\pi^2 \{3 \cos^2 \alpha - 2 + \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}, \\ f(u) &= \frac{gu^2}{4(\pi^2 - 2cu\pi \cos \alpha + c^2u^2)^{\frac{1}{2}}} = \frac{g\pi\sqrt{2}}{16c^2} \frac{18 \cos^2 \alpha - 8 + 6 \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}}{\{3 \cos^2 \alpha - 2 + \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}}. \end{aligned} \quad (78)$$

Further, when  $f'(u)$  is zero, we have

$$f''(u) = \frac{1}{4} gcu (2cu - 3\pi \cos \alpha) / (\pi^2 - 2cu\pi \cos \alpha + c^2 u^2)^{\frac{1}{2}}. \quad (79)$$

Using the formula (17) we obtain the particular group of terms from the integral (72) as

$$\zeta = -\frac{g}{2^{\frac{1}{2}} \pi \rho} \frac{u^3}{(\pi^2 - 2cu\pi \cos \alpha + c^2 u^2)^{\frac{1}{2}}} \left\{ \frac{2\pi}{f''(u)} \right\}^{\frac{1}{2}} \cos \{f(u) - \frac{1}{4}\pi\}, \quad (80)$$

in which the special value of  $u$  must be substituted.

Evaluating this expression we obtain

$$\begin{aligned} \zeta = & -\frac{g^{\frac{1}{2}}}{2^{\frac{1}{2}} \pi^{\frac{1}{2}} \rho c^{\frac{1}{2}}} \frac{\{3 \cos \alpha + (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}}{\pi^{\frac{1}{2}} (9 \cos^2 \alpha - 8)^{\frac{1}{2}} \{3 \cos^2 \alpha - 2 + \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}} \times \\ & \cos \left\{ \frac{g\pi\sqrt{2}}{16c^2} \frac{\{3 \cos \alpha + (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^2}{\{3 \cos^2 \alpha - 2 + \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}} - \frac{1}{4}\pi \right\}. \end{aligned} \quad (81)$$

This represents a system of transverse waves travelling with the originating impulse; the amplitude for a given azimuth  $\alpha$  diminishes as  $\pi^{-\frac{1}{2}}$ . On the central line, where  $\alpha$  is zero, this reduces to

$$\zeta = -\frac{2^{\frac{1}{2}} g^{\frac{1}{2}}}{\pi^{\frac{1}{2}} \rho c^{\frac{1}{2}} \pi^{\frac{1}{2}}} \cos \left( \frac{g\pi}{c^2} - \frac{1}{4}\pi \right), \quad (82)$$

corresponding to simple line waves of length suitable to velocity  $c$  on deep water, but with the amplitude factor  $\pi^{-\frac{1}{2}}$ .

Following the crest of a transverse wave we have

$$\frac{g\pi\sqrt{2}}{16c^2} \frac{\{3 \cos \alpha + (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^2}{\{3 \cos^2 \alpha - 2 + \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}} - \frac{1}{4}\pi = (2n+1)\pi, \quad (83)$$

where  $n$  is a positive integer. The crests cut the axis in points given by

$$\pi = c^2 (2n + \frac{5}{4}) \pi / g, \quad (84)$$

and cut the radial boundaries given by  $\alpha = \pm \cos 2\sqrt{2}/3$ , in the points

$$\pi = 2c^2 (2n + \frac{5}{4}) \pi / g\sqrt{3}. \quad (85)$$

Consider the variation of amplitude following a crest; we substitute for  $\pi$  from (83) in (82) and obtain

$$\zeta = \frac{\text{const.}}{(2n + \frac{5}{4})^{\frac{1}{2}}} \frac{\{3 \cos \alpha + (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}}{(9 \cos^2 \alpha - 8)^{\frac{1}{2}} \{3 \cos^2 \alpha - 2 + \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}}. \quad (86)$$

This becomes infinite at the outer boundary, when  $\alpha$  is approximately  $19^\circ 28'$ ; this is due to the failure of the method of approximation and we shall consider it later. For the present the following table of values and curve show that the approximation holds up to angles very near the limit.

Table I.

 $\zeta$  = relative amplitude, along the same crest at different azimuths.

$\alpha$ .	$\zeta$ .
0	1
6	1.03
12	1.18
18	2
19	2.9
19 15	3.5
19 27	7.5
19 28	$\infty$

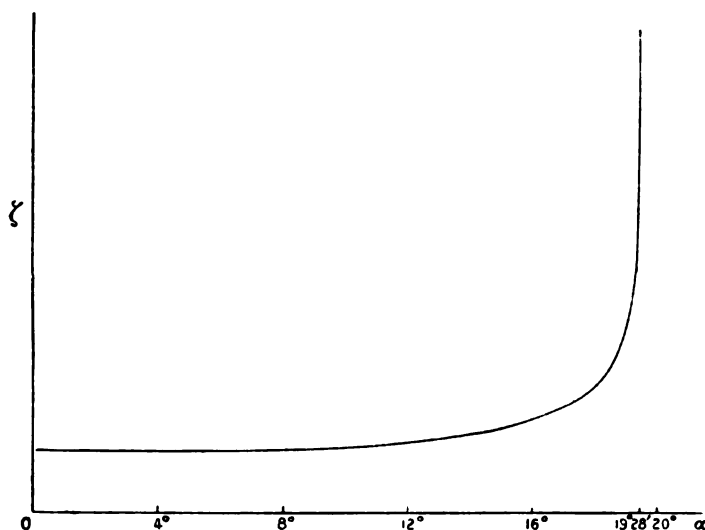


FIG. 5.

(b) *The diverging wave system.*—By taking the smaller root for  $cu$  given by (77), we obtain the system of diverging waves; we need only change the sign of the radicle in order to write down the corresponding results in this case.

The crests of the waves are given by

$$\frac{g\varpi\sqrt{2}}{16c^2} \frac{\{3 \cos \alpha - (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^2}{\{3 \cos^2 \alpha - 2 - \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}} = (2n + \frac{1}{4})\pi, \quad (87)$$

When  $\alpha$  is zero,  $\varpi$  is also zero; thus all the crests diverge from the point of impulse. Further, we have

$$\alpha = \cos^{-1} 2\sqrt{2}/3; \quad \varpi = 2c^2(2n + \frac{1}{4})\pi/g\sqrt{3}. \quad (88)$$

The law of amplitude along the same crest is given by

$$\zeta = \frac{\text{const.}}{(2n + \frac{1}{4})^{\frac{1}{2}} (9 \cos^2 \alpha - 8)^{\frac{1}{2}} \{3 \cos^2 \alpha - 2 - \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}} \cdot \quad (89)$$

In this case, and for the same reason as for the transverse waves, the expression for the amplitude tends to infinity at the outer end of each diverging crest; we shall find an approximation in the next section. But (89) becomes infinitely large for small values of  $\alpha$ . From (88) we see that  $\pi$  also becomes small, so that the approximation fails; further, we should expect the expression to become infinite near the impulse on account of its special character. We can show how the infinity disappears if we remove this cause. Consider, as an example, a finite impulse, of constant intensity over a circular area of radius  $d$  round the origin, and of zero value outside this circle. Then, as we see from (63), we shall have the same expressions as before, with a new factor given by

$$\begin{aligned} \phi(\kappa) &= \int_0^\infty f(\alpha) J_0(\kappa \alpha) \alpha d\alpha \\ &= C \int_0^d J_0(\kappa \alpha) \alpha d\alpha = C d \kappa^{-1} J_1(\kappa d). \end{aligned}$$

Now in the final group for the diverging system we have

$$\kappa = \frac{g}{8c^2} \frac{\{3 \cos \alpha - (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^2}{3 \cos^2 \alpha - 2 - \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}}.$$

Hence the additional factor due to  $\phi(\kappa)$  is proportional to

$$\frac{3 \cos^2 \alpha - 2 - \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}}{\{3 \cos \alpha - (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^2} J_1 \left\{ \frac{g d \{3 \cos \alpha - (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}}{8c^2 \{3 \cos^2 \alpha - 2 - \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}} \right\}. \quad (90)$$

When  $\alpha$  approaches zero, the argument of the Bessel's function increases indefinitely and we may use the asymptotic expansion; then (90) is proportional to

$$\frac{\{3 \cos^2 \alpha - 2 - \cos \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^{\frac{1}{2}}}{\{3 \cos \alpha - (9 \cos^2 \alpha - 8)^{\frac{1}{2}}\}^3}. \quad (91)$$

If now we multiply (89) by (91) we obtain a limiting value of the amplitude of the diverging system near the axis; it is proportional to

$$(2n + \frac{1}{4})^{-\frac{1}{2}} \{3 \cos \alpha - \sqrt{(9 \cos^2 \alpha - 8)}\}^{\frac{1}{2}},$$

and the infinity near the axis has disappeared.

(c) *The line of cusps.*—We shall consider now the infinity which occurs at the outer boundary of the two wave systems, when  $\alpha$  is  $\cos^{-1} 2\sqrt{2/3}$ . At



any point P the lines of constant phase in the two wave patterns cross at an angle  $\phi$ , which is easily seen to be given by

$$\tan \phi = \frac{1}{3} \operatorname{cosec} \alpha (9 \cos^2 \alpha - 8)^{\frac{1}{2}}. \quad (92)$$

As P approaches either radial boundary the two waves ultimately have the same direction, and they will also have the same phase when they meet; consequently an abnormal elevation is to be expected along the two outer boundaries, where the two systems unite in lines of cusps. As we see from (75), the two points A, B coincide for a point P on the line of cusps; and it is on account of this fact that the previous approximations fail for both systems. We have in fact a double root of the equation for finding the chief groups of the integral (72).

Consider the integral

$$y = \int \phi(u) \sin \{f(u)\} du, \quad (93)$$

when  $u_0$  is such that

$$f'(u_0) = 0; \quad f''(u_0) = 0.$$

Following the previous method, we have

$$f(u) = f(u_0) + \frac{1}{6} (u - u_0)^3 f'''(u_0);$$

and provided  $f'''(u_0)$  is not small, we can write the value of the group for the double root as

$$\begin{aligned} y &= \left\{ \frac{6}{f'''(u_0)} \right\}^{\frac{1}{2}} \int_{-\infty}^{\infty} \phi(u_0) \sin \{f(u_0) + \sigma^3\} d\sigma \\ &= \left\{ \frac{6}{f'''(u_0)} \right\}^{\frac{1}{2}} \phi(u_0) \sin f(u_0) \int_{-\infty}^{\infty} \cos \sigma^3 d\sigma. \end{aligned} \quad (94)$$

Now at the line of cusps the integral (72) becomes

$$\zeta = -\frac{g}{2^{\frac{1}{2}} \pi \rho} \int_0^{\infty} \frac{u^3 du}{(\pi^2 - \frac{4}{3} cu \pi \sqrt{2} + c^2 u^2)^2} \sin \frac{gu^2}{4(\pi^2 - \frac{4}{3} cu \pi \sqrt{2} + c^2 u^2)^{\frac{1}{2}}}. \quad (95)$$

And we find that

$$cu_0 = \pi \sqrt{2}$$

makes

$$f'(u_0) = 0; \quad f''(u_0) = 0;$$

$$f(u_0) = g\pi\sqrt{3}/2c^2; \quad f'''(u_0) = 3gc\sqrt{6}/2\pi^2.$$

Also we have

$$\int_{-\infty}^{\infty} \cos \sigma^3 d\sigma = \frac{2}{3} \pi / \Gamma(\frac{2}{3}).$$

Hence, substituting these values, we have

$$\zeta = -\frac{3^{\frac{1}{2}} g^{\frac{1}{2}}}{2^{\frac{1}{2}} c^{\frac{1}{2}} \rho \Gamma(\frac{2}{3}) \pi^{\frac{1}{2}}} \sin \frac{g\pi\sqrt{3}}{2c^2}. \quad (96)$$

We notice first the difference of phase of  $\frac{1}{4}\pi$  between this and the expressions for the separate systems where they cut the outer boundaries; this is analogous to the change of phase along an optical ray in passing a focus. We saw that the separate transverse and diverging crests converged towards points of equal phase on the outer boundaries given by

$$\varpi = 2c^2(2n + \frac{5}{4})\pi/g\sqrt{3},$$

but with the result given in (96) we see that the actual crests on the line of cusps are given by

$$\varpi = 2c^2(2n + \frac{3}{4})\pi/g\sqrt{3}. \quad (97)$$

The amplitude of the cusped waves diminishes at a slower rate than the transverse waves, so that their size becomes relatively more marked towards the rear of the disturbance. The amplitude of successive crests is given by (96) and (97) as

$$\zeta_{mc} = \frac{3}{2^{\frac{1}{2}}\Gamma(\frac{3}{4})(2n + \frac{3}{4})^{\frac{1}{2}}\pi^{\frac{1}{2}}c^{\frac{1}{2}}\rho} \frac{g}{c^{\frac{1}{2}}\rho}. \quad (98)$$

The amplitude of successive crests of the transverse waves where they cut the axis are given by (82) and (84), and we find

$$\zeta_{ma} = \frac{2^{\frac{1}{2}}}{(2n + \frac{1}{4})^{\frac{1}{2}}\pi} \frac{g}{c^{\frac{1}{2}}\rho}. \quad (99)$$

Taking the ratio of these two quantities we have an expression for the magnitude of the crests at the cusps compared with the transverse crests on the axis; approximately

$$\frac{\zeta_{mc}}{\zeta_{ma}} = 1.9 \frac{(2n + \frac{5}{4})}{(2n + \frac{3}{4})^{\frac{1}{2}}}. \quad (100)$$

The following table and curve show how the successive crests at the axis and outer line diminish, and exhibit their relative magnitudes for different values of  $n$ .\*

\* On August 3, 1887, Lord Kelvin delivered a lecture "On Ship Waves" before the Institution of Mechanical Engineers at Edinburgh, in which he appears to have shown a model to scale of the theoretical wave pattern produced by a ship. Only a diagram of the crest curves has been published ('Popular Lectures,' vol. 3, p. 482); the form of the crests agrees with that deduced above, except of course near the disturbance or the radial boundaries. It has, in fact, been verified that on substituting his expressions for  $x, y$  in terms of a parameter  $w$  in the present equations, the latter are satisfied identically. The law of amplitude along the waves is not stated by Lord Kelvin; as Prof. Lamb conjectures, his result seems to have been obtained by an application of the idea of group-velocity (H. Lamb, 'Hydrodynamics,' § 253, 1906).

Table II.

$n$ .	$\zeta_{ma}$ .	$\zeta_{mc}$ .	$\zeta_{mc}/\zeta_{ma}$ .
5	15	35	2.3
10	10.8	28.6	2.6
15	9	25	2.7
20	7.7	23	3
50	5	17	3.4
100	3.6	13.6	3.8

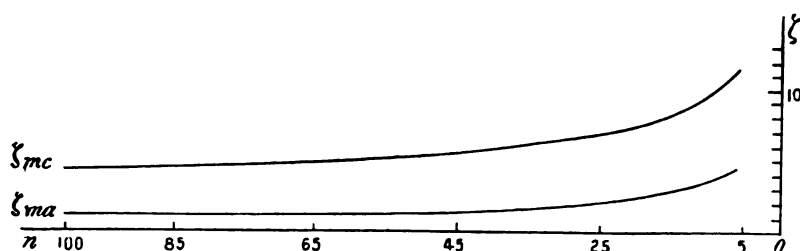


FIG. 6.

§ 14. *Point Impulse for Different Media.*

Consider a point impulse moving with uniform velocity  $c$  over the surface of a dispersive medium for which  $U$  and  $V$  are respectively the group- and wave-velocity for a value  $\kappa$  of  $2\pi/\lambda$ .

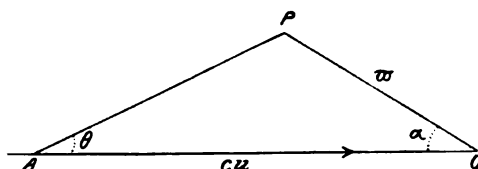


FIG. 7.

Let the disturbance from the impulse when in the neighbourhood of a point  $A$  combine so as to produce waves  $\kappa$  at  $P$  at the present moment when the impulse is at  $O$ . Then the problem of finding the possible persistent wave systems is contained in the equations

$$\frac{AP}{AO} = \frac{U}{c}, \quad c \cos \theta = V; \quad (101)$$

that is, in  $(\pi^2 - 2cu\pi \cos \alpha + c^2u^2)^{\frac{1}{2}}/u = U, \quad (102)$

$$c(cu - \pi \cos \alpha)/(\pi^2 - 2cu\pi \cos \alpha + c^2u^2)^{\frac{1}{2}} = V. \quad (103)$$

The wave pattern depends upon the character of the positive roots of these equations for  $cu$  and  $\kappa$ ; each such value of  $cu$  defines a wave system

with wave front through P at right angles to AP, and each system can be expressed in the form

$$\zeta = F(\varpi, \alpha) \cos \{ \kappa (\varpi^2 - 2cu\varpi \cos \alpha + c^2u^2)^{\frac{1}{2}} + \epsilon \},$$

with  $cu$  and  $\kappa$  as functions of  $\varpi$  and  $\alpha$ .

Suppose the medium is such that the group-velocity bears a constant ratio to the wave-velocity, that is, suppose

$$U = \frac{1}{2}(n+1)V, \quad (104)$$

where  $n$  is independent of  $\kappa$ .

Then the equations (102) and (103) lead to a quadratic for  $cu$ , namely,

$$(1-n)c^2u^2 + (n-3)cu\varpi \cos \alpha + 2\varpi^2 = 0. \quad (105)$$

Hence we have the roots

$$cu = \frac{\varpi}{2(1-n)} [(3-n) \cos \alpha \pm \sqrt{\{(3-n)^2 \cos^2 \alpha - 8(1-n)\}}]. \quad (106)$$

We shall examine some special cases.

(a)  $0 < n < 1$ .—There are two positive values of  $cu$  which are real, provided

$$\cos^2 \alpha > 8(1-n)/(3-n)^2.$$

Thus there are two wave systems, transverse and diverging, with a line of cusps corresponding to the double roots, and the whole wave pattern is included within an angle

$$2 \cos^{-1} \{ 8(1-n) \}^{\frac{1}{2}} / (3-n), \quad (107)$$

which increases with  $n$ .

The previous section on deep-water waves is the case of  $n$  zero.

(b)  $n = 1$ . This is a critical case, implying coincidence of wave-velocity with group-velocity, and consequently no dispersion.

(c)  $n = 2$ . This is the case of capillary surface waves. We see that there is only one positive root of the quadratic, and it is real for all values of  $\alpha$ ; the root is

$$cu = \frac{1}{2}\varpi \{ (\cos^2 \alpha + 8)^{\frac{1}{2}} - \cos \alpha \}. \quad (108)$$

There is only one wave system, but it extends over the whole surface; along the line of motion  $\kappa$  is zero in the rear, while in advance of the impulse it is of value suitable to simple waves moving with velocity  $c$ .

(d)  $n = 3$ . This holds for flexural waves on a plate; there is one system of waves extending over the surface, corresponding to the root  $cu = \varpi$ .

The crests, and other lines of equal phase, are given by the curves

$$\varpi \sin^3 \frac{1}{2} \alpha = \text{constant}.$$

(e) *Gravity and capillarity combined*.—The relation between  $U$  and  $V$  is

not a constant ratio in this case; we had in § 11 the expressions for the two velocities as functions of  $\kappa$ . It can be shown that in certain cases the equations for  $cu$  lead to four possible roots, giving four wave-branches through the point.

§ 15. *Point Impulse moving on Water of Finite Depth.*

With the same problem we have now, if the water is of depth  $h$ ,

$$V = \left( \frac{g}{\kappa} \tanh \kappa h \right)^{\frac{1}{2}},$$

$$U = \frac{1}{2} \left( \frac{g}{\kappa} \tanh \kappa h \right)^{\frac{1}{2}} \left( 1 + \frac{2\kappa h}{\sinh 2\kappa h} \right). \quad (109)$$

If we write

$$U = \frac{1}{2}(n+1)V,$$

$n$  varies between 0 and 1, being dependent upon the value of  $\kappa$ . We use the notation

$$p = \frac{gh}{c^2}, \quad m = \frac{\tanh \kappa h}{\kappa h}, \quad n = \frac{2\kappa h}{\sinh 2\kappa h}. \quad (110)$$

Then  $m$  and  $n$  are monotonic functions of  $\kappa$  with the following limiting values:

$$\begin{array}{lll} \kappa = 0; & m = 1; & n = 1. \\ \kappa = \infty; & m = 0; & n = 0. \end{array}$$

The two equations for  $cu$  and  $\kappa$  become

$$\frac{(\varpi^2 - 2cu\varpi \cos \alpha + c^2u^2)^{\frac{1}{2}}}{cu} = \frac{1}{2}(pm)^{\frac{1}{2}}(1+n), \quad (111)$$

$$\frac{cu - \varpi \cos \alpha}{(\varpi^2 - 2cu\varpi \cos \alpha + c^2u^2)^{\frac{1}{2}}} = (pm)^{\frac{1}{2}}. \quad (112)$$

From these we obtain

$$\cos^2 \alpha = \frac{\{1 - \frac{1}{4}pm(1+n)\}^2}{1 - \frac{1}{4}pm(1+n)(3-n)}; \quad (113)$$

$$cu = \frac{\varpi}{2(1-n)} [(3-n) \cos \alpha \pm \{(3-n)^2 \cos^2 \alpha - 8(1-n)\}^{\frac{1}{2}}]. \quad (114)$$

Combining the last two we have the values of  $cu$  as

$$cu = \frac{2\varpi}{1-n} \{1 - \frac{1}{4}pm(1+n)(3-n)\}^{\frac{1}{2}}, \quad (115)$$

or

$$cu = \varpi / \{1 - \frac{1}{4}pm(1+n)(3-n)\}^{\frac{1}{2}}. \quad (116)$$

We have two cases to consider according as  $p >$  or  $< 1$ .

(a)  $c < \sqrt{gh}$ ;  $p > 1$ .—From (114) we see that the equal values of  $cu$ ,

defining the lines of cusps within which the wave pattern lies, are given by such values of  $\kappa$  that

$$\cos^2 \alpha = \frac{8(1-n)}{(3-n)^2}. \quad (117)$$

Whatever the value of  $\kappa$ ,  $n$  can only lie between 1 and 0; hence  $\alpha$  can only lie between  $\cos^{-1} 2\sqrt{2}/3$  and  $\pi/2$ , or between  $19^\circ 28'$  and  $90^\circ$ . The smaller value is the limiting angle for deep water, when  $n$  is considered zero for all values of  $\kappa$ .

We see from (115) and (116) that the equal values of  $cu$  occur when

$$1 - \frac{1}{2}pm(1+n)(3-n) = \frac{1}{2}(1-n),$$

or when

$$m(3-n) = 2/p.$$

The greatest possible value of  $m(3-n)$  is 2; hence we have the limitation  $p > 1$ . Only in this case is there a double wave system with a line of cusps.

As  $p$  decreases to 1, that is as the velocity  $c$  approaches the critical value  $\sqrt{gh}$ ,  $m$  and  $n$  at the line of cusps both approach their limiting value 1; and at the same time the cusp angle widens out, approaching a right angle. Further, along the axis we have

$$pm = 1, \quad m = 1/p = c^2/gh.$$

Hence on the axis the transverse waves are the simple waves travelling with velocity  $c$  on water of depth  $h$ . As  $p$  decreases to 1, the wave-length increases indefinitely;  $m$ , and consequently  $n$ , approach unity on the axis.

Now if  $n$  is 1, the group-velocity  $U$  equals the wave-velocity  $V$ , and the medium is non-dispersive. Thus at the critical velocity  $c$ , equal to  $\sqrt{gh}$ , we have a source emitting disturbances and travelling at the rate of propagation of the disturbances; we see that the whole effect is practically concentrated into a line through the source at right angles to the direction of motion. This agrees with observations of ship waves when approaching shallow water at the critical velocity.\*

(b)  $c > \sqrt{gh}$ ;  $p < 1$ .—We may now have the greatest value, unity, of  $m$ ; it is easily seen that for less values of  $m$  and  $n$  the values of  $\alpha$  given by (113) become smaller.

At the outer limit we have

$$\cos^2 \alpha = 1-p, \quad \sin^2 \alpha = p = gh/c^2. \quad (118)$$

Consequently the wave pattern is contained within two lines making with the axis an angle which diminishes as  $c$  increases.

\* 'Trans. Inst. Nav. Arch.,' vol. 47, p. 353 (1905). Compare also the motion of an electron with the velocity of radiation.

Further, since equal values of  $cu$  are given by

$$m(3-n) = 2/p,$$

we see that there are no cusps, for the left-hand side cannot be greater than 2.

The values of  $cu$  given in (115) and (116) correspond to the transverse and diverging waves respectively. If we substitute (116) in equations (111) and (112) we find that they are satisfied identically; hence there is always a diverging wave system. On the other hand, if we substitute (115) we find we must have

$$pm = \frac{1-pm}{1-\frac{1}{2}pm(1+n)(3-n)}, \quad \text{or} \quad m(2-n) = \frac{1}{p}.$$

But the greatest possible value of the left-hand side is unity.

Hence there can be a transverse wave system only so long as  $p$  is greater than 1; when  $c$  exceeds  $\sqrt{gh}$ , the transverse waves disappear.

At the outer line given by

$$\sin^2 \alpha = p, \quad m = n = 1,$$

we have, for the diverging waves,

$$cu = \pi(1-p)^{-\frac{1}{2}} = \pi \sec \alpha.$$

Hence the outer line forms a wave front of the diverging wave system. We see also that the other wave fronts (lines of equal phase) are now concave to the axis, instead of being convex as when  $p > 1$ . There is no definite inner limit to the system; as the axis is approached, the wave fronts become more nearly parallel to the axis, and the wave-length diminishes indefinitely. Finally, as the velocity  $c$  is increased, the angle  $\alpha$  diminishes, and the regular waves are contained within a narrower angle radiating from the centre of disturbance.

The following tables (III) and (IV) and the curve in fig. 8 show how the angle  $\alpha$  varies as the velocity  $c$  is increased up to and beyond the critical velocity.

Table III.

$\pi h$ at cusps.	$p$ .	$\alpha$ .	$c/\sqrt{gh}$ .
		°	
10	7	19 28	0.38
8	5.4	19 28	0.42
6	4	19 29	0.5
5	3.3	19 30	0.55
4	2.7	19 37	0.6
3	2	20 18	0.7
2	1.5	23 42	0.82
1	1.18	39 19	0.92
0.5	1.08	59 27	0.96
0.2	1.01	78	0.99
0	1	90	1

$$\alpha = \cos^{-1} \sqrt{8(1-p)/(3-p)}.$$

Table IV.

$p.$	$\alpha = \sin^{-1} \sqrt{(p)}.$	$c/\sqrt{(gh)}.$
0.99	84	1.006
0.5	45	1.41
0.33	35	1.73
0.25	30	2
0.11	19 28	3

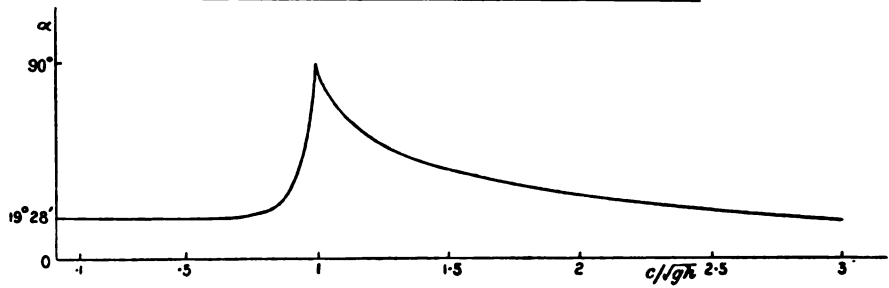


FIG. 8.

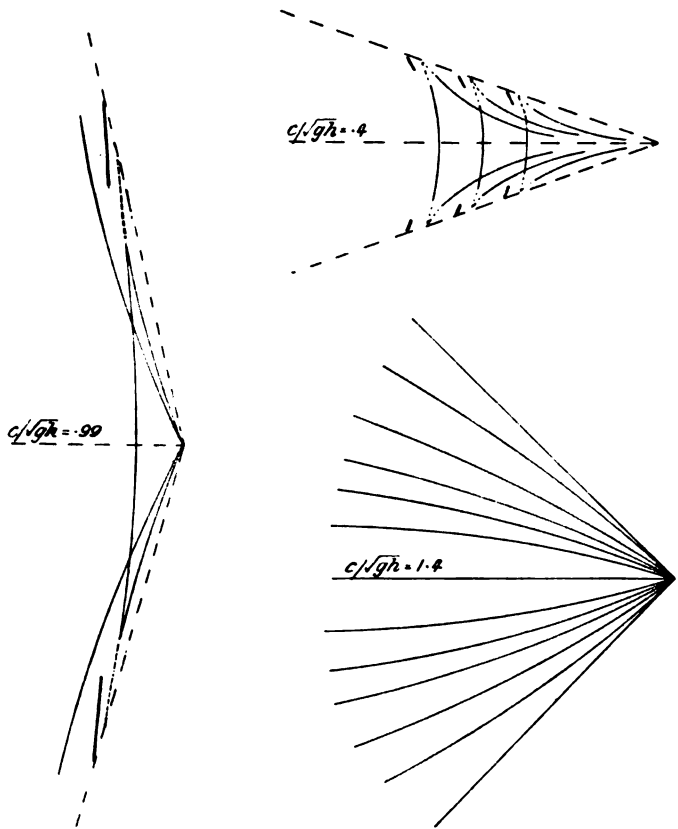


FIG. 9.



With the help of these results, sketches are given in fig. 9 to represent the change in the wave pattern, as the critical velocity is approached and passed.

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*On the Generation of a Luminous Glow in an Exhausted Receiver moving near an Electrostatic Field, and the Action of a Magnetic Field on the Glow so produced; the Residual Gases being Oxygen, Hydrogen, Neon, and Air.—Part 3.*

By FREDERICK JOHN JARVIS-SMITH, M.A. (Oxon), F.R.S.

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(1) A silica bulb, similar to those employed in the experiments described at p. 214, 'Roy. Soc. Proc.,' A, vol. 81, was rotated four to five revolutions per second; the degree of exhaustion was similar to that reached in the former experiments, the residual gas being oxygen. The inductor was charged gradually, until the bulb glowed; then slowly discharged through a piece of damped thread, until the glow entirely died out; the graduated electroscope being observed during the slow discharge. On establishing the magnetic field, the brilliant glow was at once restored. This phenomenon could be repeated at any time with certainty. In some experiments the south pole was effective, the north pole not so. This was probably connected with the fact that the north pole deflected the glow away from the stem of the bulb, which was the axis of rotation, and thus in contact with outside bodies.

(2) A silica bulb, the residual gas being air, when similarly treated, glowed; but the magnetic effect was less marked than when oxygen was the residual gas.

(3) A bulb of *glass* was next rotated; the inductor being charged as in the former experiment; the glow was very much less than when a silica bulb was used. The glow was deflected by the magnetic field, but not appreciably increased. Even when the inductor was charged to 3000 volts the glow was feeble.

(4) In order to discover how far the residual gas in the exhausted bulb affected the phenomena, I determined to contrast the effects produced in silica bulbs when neon or oxygen were the residual gases in the bulbs.

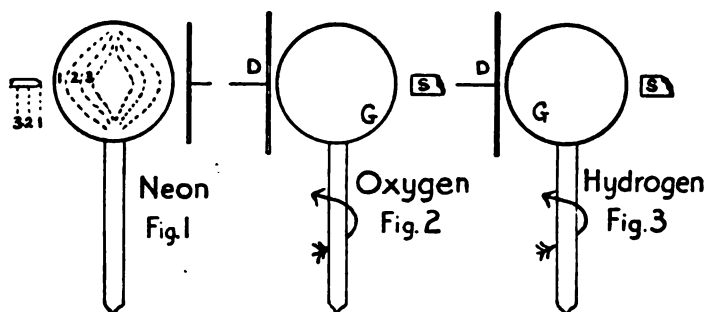
Sir William Ramsay very kindly offered to prepare me a bulb, in which the residual gas was neon.

*Neon Bulb tested for After-glow.*

(5) A silica bulb was exhausted, the residual gas being neon, and placed between disc and point electrodes of an induction coil, and subjected to a discharge similar in all respects to that used in the experiment in which the residual gas was oxygen. No after-glow was produced, as was the case when either air or oxygen was the residual gas.

(6) The neon bulb, while subjected to the discharge, was filled with a reddish glow, which changed its shape with a change of distance of the pointed electrode. In the figure (fig. 1) the dotted curves show roughly the shape of a section through a cap of glow, and the numbers refer to the relative positions of the pointed electrode and the pairs of curve-shaped caps of glow. When the electrode was within 5 mm. of the surface of the bulb, the radius of the cap of glow became small and brilliant exactly opposite the electrode. But as the point was moved away the radius of curvature of the cap became greater.

The neon bulb was next mounted in the rotation apparatus in an electrostatic field, and when treated in exactly the same manner as the oxygen glow-bulbs it gave but little glow, but what it gave was of a reddish colour; also the neon glow was but feebly affected by the magnetic field.



(7) A silica glow-bulb, the residual gas being air, was rotated, as in the previous experiments.\* The inductor was charged to 800 volts, and placed at such a distance from the bulb that it did not show any glow. Then on establishing a *magnetic field*, in which the bulb rotated, it *glowed brightly*, the glow being either to the right or left hand, according to the polarity of the magnet.† The glow varied with the strength of the magnetic field. The phenomenon is very remarkable, but at present sufficient evidence has not been obtained to suggest an explanation. The effect was not altered

\* 'Roy. Soc. Proc.,' p. 216, A, vol. 80.

† *Loc cit.*

when a sheet of non-magnetic material was interposed between the bulb and the magnet.

(8) Glass bulb, residual gas hydrogen. A glass bulb in which the residual gas was hydrogen was rotated in the same manner as the glow-bulbs already described. Since hydrogen passes through silica at a high temperature, a glass bulb was used, so that the exhaustion might not be affected by the process of sealing-off the tube of the bulb. The position of maximum glow in the case of glow-bulbs in which hydrogen and oxygen are the residual gases is shown at G in figs. 2 and 3, in which D is the inductor charged negative, and S the south pole of magnet.

(9) The effect of a magnetic field on the generation of electricity, by friction of a silica glow-bulb against a camel-hair brush, or the finger. A silica glow-bulb B, fig. 4 (the residual gas being air), was rotated 30 times

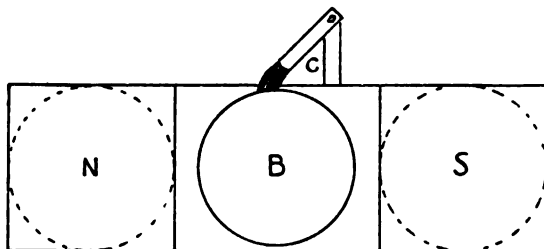


FIG 4

per second, between the poles of a large electro-magnet, of the type used in diamagnetic experiments. The pole pieces, N, S, were flat, and the field between them practically straight (6 cm.). The revolving bulb was in contact with a stiff camel-hair brush C, the length of the flexible hair being about 5 mm. This brush was held by a metal arm midway between the poles of the electro-magnet. The pressure of the brush on the bulb was so adjusted that not the slightest glow was visible; but the instant the magnetic field was established the bulb glowed brightly, and ceased to glow the instant the magnetic field was removed by opening the magnetising circuit. The experiment was repeated, at short intervals, by me and my assistant, during one and a-half hours, when the same phenomena exactly repeated themselves. The intensity of the magnetic field was about 1050 to 3000 c.g.s. units, by the Kelvin long coil ballistic method. The glow was produced, in a slight degree, by a lower intensity of magnetic field. The same effects were produced by using a finger as a rubber, instead of the brush. It was noticed that flashes of light passed through the tubular stems of the glow-bulbs, to a conductor touching their ends; this appears to indicate that the matter within the bulb is electrically charged, as well as the surface of the bulb.

(10) The effect of a magnetic field on a glow-bulb after the rubber had been removed. A silica glow-bulb was rotated, as in section (9). The camel-hair rubber, after being in contact with the bulb, was removed, and no glow was visible; but on establishing the magnetic field (about 800 c.g.s. units intensity), the bulb instantly glowed brightly, the glow lasting in some cases eight minutes before it died out.

(11) When pointed pole pieces were used on either side of the rotating bulb, a bright equatorial band about 5 mm. wide of greenish glow was generated, the rest of the glow in the bulb being reduced in intensity.

(12) None of the effects described in sections (9), (10), (11) could be produced in an unexhausted bulb.

(13) The experiments described in this paper illustrate the profound change which takes place in the behaviour of a moving static induction of electricity when the bulb in which it occurs is in a magnetic field, and show how the action of the magnetic field on the electric motion in the residual gas is modified by the nature of the gas employed. In the case of hydrogen, the maximum glow is approximately situated, in the bulb, at an angle of  $45^\circ$  from the maximum glow when oxygen is the residual gas. When air, oxygen, or neon are the residual gases, the positions of the glow with respect to the magnet pole are similar.

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*On the Osmotic Pressures of Aqueous Solutions of Calcium  
Ferrocyanide. Part I.—Concentrated Solutions.*

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(Abstract.)

The principal aim of this paper was to test the nearness of possible approach to complete osmotic efficiency for strong solutions. To this end the experimental verification of the exact physical equation given by A. W. Porter\* was undertaken, a membrane having been constructed which could withstand osmotic pressures of calcium ferrocyanide up to 150 atmospheres without any sensible percolation of the solution. It was found, notwithstanding many precautions, that the formula would not verify within about 3 per cent. But further consideration showed that this formula must refer to osmotic pressures *in vacuo*, whereas the experiments were necessarily conducted in air at atmospheric pressure. Reconstructing the argument in terms of ideal osmotic partitions impermeable to air but permeable to the solution, the equation was modified so as to apply strictly to the quantities involved in the experimental determinations, which required the addition of the atmospheric pressure to the limits in the first and third of the integrals concerned in it.

The final results are given in the following table :—

I. Weight concentration.	II. " Unmodified " equation.	III. " Modified " equation.	IV. Observed equilibrium pr.
49·966	135·04 atmos.	131·45 atmos.	130·66 atmos.
47·219	116·05 "	112·96 "	112·84 "
42·889	88·99 "	86·61 "	87·09 "
39·503	72·54 "	70·61 "	70·84 "
31·388	42·38 "	41·24 "	41·22 "

From the concordance of these numbers, it may fairly be deduced that the membrane establishes, unambiguously, even with concentrated solutions, the full theoretical osmotic pressures, for the thermodynamic relations, at these high pressures, are completely verified.

\* 'Roy. Soc. Proc.,' A, vol. 79, 1907, p. 519.

*On Anomalies in the Intensity in Diffracted Spectra.*

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Professor Wood\* has found that the spectra of an incandescent lamp formed by a grating can have bright and dark lines in them. These occur at the same place in each order of spectrum, and move through the spectrum when the inclination of the grating is altered. The phenomenon has been investigated by Rayleigh,† who discusses the case of diffraction by a grooved reflecting surface. On account of the analytical difficulties he uses approximations. In the present paper a theoretical grating is discussed, the phenomena of which can be investigated accurately, an advantage that is, however, coupled with the drawback that we cannot feel certain how far the phenomena agree with those of the ordinary metallic reflection grating.

A theorem that gives the sum of certain infinite series in a finite form, and transforms others into new series, is found in § 5.

2. Let the grating consist of an infinite number of very thin rods of specific inductive capacity unity, each electrified to a line density  $\sigma$  and capable of oscillating, lying at equal distances  $a$  parallel to each other in a plane. We take the axis of  $z$  along one of the rods, that of  $x$  in the plane of the grating, and that of  $y$  perpendicular to that plane.

Let the incident waves be propagated in a direction parallel to the plane of  $xy$  and making an angle  $\theta$  with the axis of  $y$ , and let the electric force be

$$\exp ip(t - y \cos \theta - x \sin \theta).$$

The displacement of a rod is

$$\delta = A \exp ip(t - x \sin \theta),$$

where  $A$  is complex, unless the phase of the displacement of the rod is the same as that of the wave incident on it.

Since the diffracted waves depend only on the motion of the rods, and are given by a formula without peculiarities, the features that characterise these waves will depend only on the behaviour of the quantity  $A$ .

3. We first consider the case where the electric vibration in the incident waves is parallel to the rods. The rods here vibrate longitudinally. The forces acting on one of them are: i, a force of restitution partly of mechanical origin and partly due to the repulsions of the other rods, say,  $b\delta$ ; ii, a force of

\* R. W. Wood, 'Phil. Mag.,' Ser. 6, vol. 4, 1902, p. 396.

† Lord Rayleigh, 'Roy. Soc. Proc.,' A, vol. 79, 1907, p. 399.

electrical origin due to the rod itself and in phase with the motion, which produces an apparent increase in the inertia of the rod; iii, a similar force in quadrature with the motion; iv, another force, due to the action of all the other rods. The work done by the third force is equal to the energy radiated by an isolated rod, and hence the force is easily shown to be of the form  $-ikAp^2\sigma^2$ , where  $k$  is a constant.

4. In order to find the value of the last force, we must find the field due to the oscillating rods. Now, the components of the electric force at  $(x, y, z)$  due to an oscillating charge  $\sigma d\zeta$  situated at  $(0, 0, \zeta)$  are

$$X = d^2\Pi/dx\,dz, \quad Y = d^2\Pi/dy\,dz, \quad Z = d^2\Pi/dz^2 + p^2\Pi,$$

where

$$\Pi = A\sigma d\zeta e^{-i\rho p}/\rho,$$

$\rho$  being the distance of  $(x, y, z)$  from  $(0, 0, \zeta)$ . On integrating with respect to  $\zeta$ , we find that  $X, Y$ , and the first term of  $Z$  vanish, and we have

$$Z = 2A\sigma p^2 \int_0^\infty \Pi d\zeta = 2A\sigma p^2 \int_0^\infty d\rho e^{-i\rho p}/\sqrt{(\rho^2 - r^2)},$$

or if  $\rho = ru$ ,

$$= 2A\sigma p^2 \int_1^\infty du e^{-i\rho r u}/\sqrt{(u^2 - 1)} = A\sigma p^2 \pi \{-iJ_0 pr - \tau_0 pr\},^*$$

where  $\tau_0$  is that second solution of Bessel's equation, the graph of which at infinity consists of waves of the same amplitude as those of the Bessel's function, but in quadrature with them. Hence the mechanical force exerted on the rod by the other rods is

$$\begin{aligned} \Sigma A\sigma^2 p^2 \pi \{-iJ_0 pr - \tau_0 pr\} 2 \cos(px \sin \theta) \\ = -2A\sigma^2 p^2 \pi \Sigma_1 \{iJ_0 npa + \tau_0 npa\} \cos(npa \sin \theta), \end{aligned}$$

since  $r = x = na$ .

5. Consider the expression

$$\frac{1}{2} \int_0^\infty f(\lambda) \{1 + \Sigma_1 c^n \cos(\lambda - \alpha) nu + \Sigma_1 c^n \cos(\lambda + \alpha) nu\} d\lambda.$$

Its limit when  $c = 1$  is

$$\frac{1}{2} \int_0^\infty f(\lambda) d\lambda + \Sigma_1 \cos n\alpha u \int_0^\infty f(\lambda) \cos n\lambda u d\lambda. \quad (A)$$

Also in the limit,  $\frac{1}{2} + \Sigma c^n \cos(\lambda - \alpha) nu$  vanishes unless  $(\lambda - \alpha)u$  is a multiple of  $2\pi$  (say  $2m\pi$ ) and its integral with respect to  $\lambda$  from a value slightly less to one slightly greater than one of the critical values is  $\pi/u$ . Hence the series also is

$$(\pi/2u) \Sigma [f(2m\pi/u + \alpha) + f(2m\pi/u - \alpha)], \quad (B)$$

\* Gray and Mathews, 'Bessel's Functions,' p. 230, Ex. 18.

where only positive values of the argument are to be taken. The function  $f(\lambda)$  need not be continuous. The value at any point of discontinuity is to be taken to be the mean of the values on either side, and  $f(0)$  is to be replaced\* by  $\frac{1}{2}f(0)$ . If  $f(\lambda)$  vanishes unless  $\lambda$  lies between certain limits, we may reduce the integral to one taken between these limits, and in the Series B take only those terms the arguments of which lie between these limits.†

6. Putting  $f(\lambda) \equiv 2/\pi\sqrt{(1-\lambda^2)}$ ,  $u = pa$  and  $a = \sin \theta$ ,

$$\sum_1^{\infty} \cos(npa \sin \theta) J_0 npa \\ = \frac{1}{pa} \sum \left[ \frac{1}{\sqrt{\{1-(2m\pi/pa + \sin \theta)^2\}}} + \frac{1}{\sqrt{\{1-(2m\pi/pa - \sin \theta)^2\}}} \right] - \frac{1}{2}.$$

In the case of the  $\gamma_0$  functions, take the integral in the first instance from 0 to  $\kappa$ . Then,

$$\frac{2}{\pi} \sum_1^{\infty} \cos(npa \sin \theta) \int_1^{\kappa} \frac{\cos \lambda npa}{\sqrt{(\lambda^2 - 1)}} d\lambda \\ = \frac{1}{pa} \sum \left[ \frac{1}{\sqrt{\{(2m\pi/pa + \sin \theta)^2 - 1\}}} + \frac{1}{\sqrt{\{(2m\pi/pa - \sin \theta)^2 - 1\}}} \right] - \frac{\log 2\kappa}{\pi},$$

but

$$\frac{\log 2\kappa}{\pi} = \frac{1}{\pi} \log 2 + \left(1 + \frac{1}{2} + \dots + \frac{1}{\kappa} - \gamma\right) / \pi \\ = \frac{-\gamma + \log 2}{\pi} + \frac{1}{\pi} + \frac{1}{2\pi} + \dots + \frac{1}{\kappa\pi},$$

where we may add or take away any finite number of terms at the end of the series. Hence, making  $\kappa = \infty$ , our sum is

$$\sum \left[ \frac{1}{\sqrt{\{(2m\pi + pa \sin \theta)^2 - p^2 a^2\}}} + \frac{1}{\sqrt{\{(2m\pi - pa \sin \theta)^2 - p^2 a^2\}}} - \frac{1}{m\pi} \right] \\ + \frac{\gamma - \log 2}{\pi}.$$

Equating now the force due to the incident waves to the sum of the other forces and the reversed acceleration multiplied by the mass, we have

$$\sigma = A \left\{ -b - kp^2 \sigma^2 i - 2\sigma^2 p^2 \pi i \sum \left[ \{p^2 a^2 - (2m\pi + pa \sin \theta)^2\}^{-\frac{1}{2}} \right. \right. \\ + \{p^2 a^2 - (2m\pi - pa \sin \theta)^2\}^{-\frac{1}{2}} \left. \right] + \sigma^2 p^2 \pi i \\ + 2\sigma^2 p^2 \pi \sum \left[ \{(2m\pi + pa \sin \theta)^2 - p^2 a^2\}^{-\frac{1}{2}} + \{(2m\pi - pa \sin \theta)^2 - p^2 a^2\}^{-\frac{1}{2}} - \frac{1}{m\pi} \right] \\ + 2\sigma^2 p^2 (\gamma - \log 2) \\ \left. + p^2 M \right\}, \quad (1)$$

where  $M$  is the mass per unit length of a rod.

\* Cf. Dirichlet's investigation of Fourier's Series.

† If we take  $f(\lambda) \equiv \exp(-k\lambda^2)$ , we get a theorem in Elliptic Functions.



The summations are in each case for integral values of  $m$ . In the first case such values are to be taken as make the ( ) neither negative nor greater than  $pa$ . In the second case the ( ) are not to be less than  $pa$ , the  $m$  in  $1/m\pi$  is to range from 1 to  $\infty$  and each [ ] is to be considered as one term (this will require the omission of one or two of the three terms from some of the [ ] at the beginning of the series).

7. Now let  $p$  increase through a value

$$p = 2m\pi/a (1 \pm \sin \theta). \quad (2)$$

The first  $\Sigma$  becomes infinite when  $p$  is infinitesimally greater than this value, and the second  $\Sigma$  becomes infinite when  $p$  is infinitesimally less than it. In either case  $A$  vanishes. Hence each of the spectra composing the diffracted light will have a dark line for any such value of  $p$ .

Again, if  $b$  is large, so that the natural period of a rod is small, there will be a value of  $p$ , rather less than that which makes the second  $\Sigma$  infinite, for which the real part of the coefficient of  $A$  vanishes. In this case the value of  $A$  will be exceptionally large. We have, in fact, a case of resonance. Hence in each spectrum there will be a bright line near to the dark one and on the red side of it.

8. We must now consider the case where the electric force in the incident waves is perpendicular to the rods. First let the rods be capable of vibration only in their own plane. The electric force due to a rod is now

$$\left(p^2 + \frac{d^2}{dx^2}\right) 2\sigma A \int_1^\infty \frac{\exp(-ipru)}{\sqrt{(u^2-1)}} du.$$

This is to be multiplied by  $\cos(pr \sin \theta)$  and summed for all values of  $r$  given by  $r = na$  (excluding  $n = 0$ ). Now if  $K(pr)$  is any Bessel's function of zero order,  $\left(p^2 + \frac{d^2}{dx^2}\right) K(pr)$  is equal to  $r^{-\frac{1}{2}}$  multiplied by a finite quantity (for the case  $r = 0$  is excluded). Hence the series in question converges and is finite for all values of  $p$ . Hence there are no singularities of the kind that were discussed in § 7.

9. Next let the rods be capable of vibration only at right angles to their plane, the incident waves being as before. The force due to a rod is now

$$\left(p^2 + \frac{d^2}{dy^2}\right) \Pi = -\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right) \Pi = -\frac{d^2 \Pi}{dx^2},$$

where  $\Pi$  is now  $2\sigma A \int_1^\infty \frac{e^{-ipru}}{\sqrt{(u^2-1)}} du$ . Therefore we get the force in question by subtracting that found in § 8 from that found in § 6.

The former force gives rise to no singularities, and those that the latter gives rise to have already been discussed. There is, however, one new

feature, for the left-hand side of equation (1) now is  $\sigma \sin \theta$ , with the result that there are no diffracted waves if  $\theta = 0$ .

Finally, let the rods be free to vibrate in any direction. If the force of restitution is opposite to the displacement the diffracted wave is the sum of those found in §§ 8, 9, and no new singularities occur. If the force of restitution is a linear vector function of the displacement the same result seems to hold, but there may be a diffracted wave in the case of perpendicular incidence.

10. We must next consider the effect of change in the angle of incidence of the light. As  $\theta$  increases one of the values of  $p$  given by (2) increases and the other decreases; hence one set of dark lines moves towards the blue end of the spectrum and the other towards the red, in each case accompanied more or less closely by the corresponding bright lines.

11. We cannot obtain mechanical systems that have frequencies comparable with that of light. However, when a conducting rod is placed in an electric field perpendicular to it, a displacement of electricity occurs in it which makes it behave in much the same way as if it were a rigidly electrified rod displaced bodily, and the frequency will be comparable with that of light if the diameter of the rod is comparable with the wave-length of light. The damping due to radiation is also high, and therefore in the case of a wire grating exposed to waves in which the electric force is perpendicular to the wires, we should expect to find the dark lines but not the bright ones. The kind of grating that seems most favourable to the production of the latter is one in which the grooves are narrow cracks, such as a diamond makes in glass when used to "cut" it. Possibly, however, the cracks in a grating made in the way suggested would be so narrow that there would be no appreciable reflection at them, even at very oblique incidences.

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*On the Refraction and Dispersion of Krypton and Xenon and  
their Relation to those of Helium and Argon.*

By C. CUTHBERTSON, Fellow of London University, University College; and  
M. CUTHBERTSON.

(Communicated by Prof. F. T. Trouton, F.R.S. Received September 28,—  
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By the kindness of Sir William Ramsay and Prof. R. B. Moore, we have been enabled to measure the refractive indices of krypton and xenon with much larger quantities of these gases than were available at the time of their first isolation. The method of preparation of the gases will be given by Prof. Moore in a paper about to be presented to the Chemical Society. The procedure followed in determining the indices is described in a paper lately published by the Royal Society,\* and need be only briefly recapitulated.

Jamin's refractometer was used, and the source of light was, for the refraction, a Bastian mercury lamp, and for the dispersion, a Nernst lamp in conjunction with a fixed-deviation spectroscope. In measuring the dispersion, one of the two tubes was filled with the gas in question, and the other with air at such a pressure that the optical lengths of path of the two interfering rays were approximately equal. The light was then continuously changed from  $\lambda = 6500$  to  $\lambda = 5000$ , and the change in the position of the centre of a given bright band was observed in a telescope fitted with a micrometer eyepiece. The distance on the same scale between the centres of two adjacent bright bands of known wave-length (generally  $\lambda = 5461$ ) was also noted. These observations constituted the point of departure. The pressure of the gas in one tube was then altered till a convenient number of bands of wave-length 6500 (usually 85) had passed in one direction; and, next, the pressure of air in the other tube was altered till the same number of bands had passed in the contrary direction. The wave-length of the light was then changed from the first wave-length to the second, and the movement of the centre of the bright band under observation was again noted.

Suppose that this movement is  $a$  divisions of the micrometer, and that the distance between the centres of two adjacent bright bands of wave-length 5461 is  $b$  divisions. Let  $N_R$  be the number of bands of wave-length 6500 which pass and repass,  $N_D$  the number of bands of wave-length 5000 which would have been observed with light of this wave-length if the pressure of

\* "On the Dispersion of Gaseous Mercury, Sulphur, Phosphorus, and Helium," by C. Cuthbertson and E. P. Metcalfe, 'Roy. Soc. Proc.' A, vol. 80, p. 411, 1908.

the air alone had been changed, and  $N_V^G$  the corresponding number if the pressure of the gas alone had been changed.

Then what is observed is that the relative path retardation

$$5000N_V^A - 5000N_V^G = \frac{a}{b} 5461,$$

which may be written

$$\frac{5000N_V^A - 6500N_R}{\lambda N_A} - \frac{5000N_V^G - 6500N_R}{\lambda N_A} = \frac{a}{b} \cdot \frac{5461}{\lambda N_A},$$

where  $\lambda N$  is the path retardation for any wave-length. And since  $\lambda N$  is in each case proportional to  $\mu - 1$ , this equation becomes

$$\frac{\mu_V^A - \mu_R^A}{\mu_A^A - 1} - \frac{\mu_V^G - \mu_R^G}{\mu_A^G - 1} = \frac{a}{b} \frac{5461}{\lambda N_A}.$$

The first term on the left is the dispersive power of air, which is known, and since  $\lambda N_A$  is observed, the dispersive power of the gas can be calculated.

*Krypton*.—About 100 c.c. of gas at normal temperature and pressure were employed. The refractive index for the mercury green ray was determined six times, each determination being the mean of two readings of 100 bands, in one of which pressure was rising and in the other falling, so as to eliminate the effect of a drift of zero. The following are the values obtained :—

No. of experiment.	$(\mu - 1) 10^6$ $\lambda = 5461.$
1 .....	428·71
2 .....	428·64
3 .....	428·86
4 .....	428·15
5 .....	428·92
6 .....	428·57
Mean of 1, 2, 3, 5, and 6 ...	428·74

The divergence shown in the fourth experiment was accounted for, and it may be neglected. The others agree to one part in a thousand, and their mean may be accepted.

The dispersion was calculated from seven experiments :—

No. of experiment.	Excess of dispersive power of Kr over that of dry air.
1 .....	0·00208
2 .....	0·00204
3 .....	0·00213
4 .....	0·00207
5 .....	0·00243
6 .....	0·00191
7 .....	0·00220
Mean.....	0·00212

The dispersive power of air has been investigated several times, but, unfortunately, the results are not very concordant. The following table shows the principal determinations, the difference of refractivity between  $\lambda = 6500$  and  $\lambda = 5000$ , and the fraction expressing the dispersive power calculated for these limits.

Table I.

Observers.	Refractive index of air. $\mu - 1$ .	$\mu_{5000} - \mu_{6500}$ .	Dispersive power. $\frac{\mu_{5000} - \mu_{6500}}{\mu_{\infty} - 1}$ .
Kayser and Runge...	$0.00028817 + \frac{1.316}{\lambda^2} + \frac{31600}{\lambda^4}$	0.00000246	0.0085481
Mascart .....	$0.00028715 \left(1 + \frac{5.8}{\lambda^2 10^{11}}\right)$	0.00000273	0.00947
Scheel .....	$0.00028705 \left(1 + \frac{5.67}{\lambda^2 10^{11}}\right)$	0.00000266	0.00926
Perreau .....	$0.0002879 \left(1 + \frac{5.6}{\lambda^2 10^{11}}\right)$	0.00000263	0.00914

The figures of Mascart, Scheel, and Perreau, are so nearly alike that the truth probably lies near them, and we select those of Scheel. According to him, the dispersive power of air between the limits  $\lambda = 6500$  and  $\lambda = 5000$  is 0.00926; and this, added to the excess of the dispersive power of krypton over air (0.00212) gives 0.01138.

If the dispersion of krypton is expressed in the form

$$\mu - 1 = a(1 + b/\lambda^2),$$

we have, therefore, 
$$b \left( \frac{1}{5000^2} - \frac{1}{6500^2} \right) = 0.001138.$$

And from the refractivity for  $\lambda = 5461$  we have

$$a \left( 1 + \frac{b}{5461^2} \right) = 0.0004287.$$

Hence 
$$\mu - 1 = 0.0004189 \left( 1 + \frac{6.97}{\lambda^2 10^{11}} \right).$$

It must be remembered that these figures are for the gas at normal temperature and pressure, without making allowance for the fact that the molecule is monatomic. In making comparison for an equal number of atoms ( $\text{Kr}_2$ ), instead of an equal pressure, the value of  $a$  must be doubled.

In the first four experiments, readings were taken of the movement of the bands at the point  $\lambda = 5800$ . The following table shows the results:—

Table II.

	Dispersive power.		
	$\lambda = 6500$ to $\lambda = 5800$ .	$\lambda = 5800$ to $\lambda = 5000$ .	$\lambda = 6500$ to $\lambda = 5000$ .
Excess of krypton over air .....	0·000707	0·001365	0·002072
Air (Scheel).....	0·003420	0·005840	0·00926
Krypton .....	0·004127	0·007205	0·001133
$b$ (calculated) .....	6·9	7·0	6·937

It will be observed that the values of  $b$  calculated from the two sets of figures agree well.

*Xenon*.—About 120 c.c. of this gas were employed. The following table shows the results of four determinations of the refractive index for the green mercury line:—

No. of experiment.	$(\mu - 1) 10^6$ .
1 .....	705·72
2 .....	705·30
3 .....	705·19
4 .....	705·74
Mean 705·49	

The dispersion was calculated from eight experiments.

No. of experiment.	Excess of dispersive power over dry air.
1 .....	0·00645
2 .....	0·00732
3 .....	0·00800
4 .....	0·00738
5 .....	0·00750
6 .....	0·00749
7 .....	0·00680
8 .....	0·00758
Mean .....	0·00730
Add dispersive power of air = 0·00926	
0·01656	

From these figures we find that the refractive index of xenon doubled ( $X_2$ ) is expressed by the formula

$$\mu - 1 = 0\cdot0013646 \left( 1 + \frac{10\cdot14}{\lambda^2 10^{11}} \right).$$

With regard to the accuracy of these results, it is only necessary to observe briefly that it depends on four principal factors:—

(1) The purity of the gas, which is dealt with in Prof. Moore's paper, to which reference has been made.

(2) The correctness of the assumed value for the dispersion of air: as shown above, this is probably trustworthy within 2 or 3 per cent.

(3) The experimental errors, which can be judged from the figures given. We think that they do not amount to much more than in the case of air.

(4) The adequacy of Cauchy's formula: the figures given for the intermediate values of the dispersion of krypton show that the degree of accuracy attained was not sufficient to test this point.

*Relative Refractivities of the Inert Gases.*

*Helium.*—The index of helium has recently been determined by four sets of observers. Their results are as follows, and are for  $\text{He}_1$ :—

Table III.—Refraction and Dispersion of Helium.

$\mu - 1.$	Observers.
$0.00003478 \left(1 + \frac{2.2}{\lambda^2 10^{11}}\right)$	W. Burton, 'Roy. Soc. Proc.,' A, vol. 80, 1908, p. 390.
$\lambda.$	
$0.0579 \left. \begin{array}{l} \right\} 0.000034384$	Kurt. Herrmann, 'Ber. d. Deu. Phys. gesell.,' 1908, part 5.
$0.0576 \left. \begin{array}{l} \right\} 0.000034525$	
$0.05461 \left. \begin{array}{l} \right\} 0.000035332$	
$0.04359 \left. \begin{array}{l} \right\}$	
$0.06676 \quad 0.0000346$	K. Scheel and Schmidt, <i>ib.</i>
$0.05876 \quad 0.0000340$	
$0.05790 \quad 0.0000338$	
$0.05770 \quad 0.0000338$	
$0.05016 \quad 0.0000336$	
$0.04358 \quad 0.0000342$	
$\infty \quad 0.0000340 \pm 2$	
$0.0000347 \left(1 + \frac{2.4}{\lambda^2 10^{11}}\right)$	Cuthbertson and Metcalfe, 'Roy. Soc. Proc.,' A, vol. 80, 1908, p. 411.

The first and last sets of figures agree very well; the others do not. We select those of Mr. Burton for comparison with our results.

*Neon.*—We regret that we have not been able to obtain a sufficient quantity of pure neon to enable us to measure its dispersion. The only value with which we are acquainted is that of Ramsay and Travers for white light;  $\mu = 1.0000687$ , while, for air,  $\mu = 1.000293$ .

*Argon.*—Mr. Burton has also redetermined the index of argon, finding for  $A_1$  the value

$$\mu - 1 = 0.0002792 \left(1 + \frac{5.6}{\lambda^2 10^{11}}\right).$$

On several occasions it has been shown how closely the refractivities of these gases approach to the ratios of 1, 2, 8, 12, and 20. We are now able to compare the values for infinite wave-lengths as calculated from Cauchy's formula, and find that the coincidence is still more striking. The original figures of Ramsay and Travers are shown in column 2. They are for white

light. In columns 5, 6, and 7 the figures for neon are the old values for white light multiplied by two.

Table IV.—Relative Refractivities of the Inert Gases for infinite Wave-lengths.

1.	2.	3.	4.	5.	6.	7.
	Ramsay and Travers, 1901 (molecular). $(\mu-1) 10^6$ .	Empiric ratios.	Divergence from Col. 3, per cent.	Revised values (atomic). $(\mu-1) 10^6$ .	Col. 5 divided by Col. 3.	Divergence per cent. from Col. 3, revised values.
Helium .....	36.3	1	+2.3	69.56	69.56	-0.34
Neon .....	68.7	2	-3.2	(137.4)	68.7	-1.6
Argon .....	284	8	—	558.4	69.8	— standard
Krypton .....	425	12	-0.2	837.8	69.8	0.0
Xenon .....	689	20	-3.0	1364.6	68.23	-2.25

*Relative Dispersive Power of the Inert Gases.*

In his paper, cited above, Mr. Burton compares the dispersive powers of helium and argon with hydrogen, and points out that when they are expressed in the form  $\mu-1 = a(1+b/\lambda^2)$  the values of  $a/b$  are roughly in the ratios of 1, 3, and 2 respectively. It is now possible to extend this comparison to krypton and xenon.

The following figures show that the coincidence fails in these cases. If the value of  $a/b$  for helium be taken as 1 and that for argon as 3, the values for krypton and xenon are not in the ratios of simple integers. It should also be observed that Mascart's value of  $b$  for hydrogen, adopted by Burton for comparison, is not supported by the determinations of other observers.\*

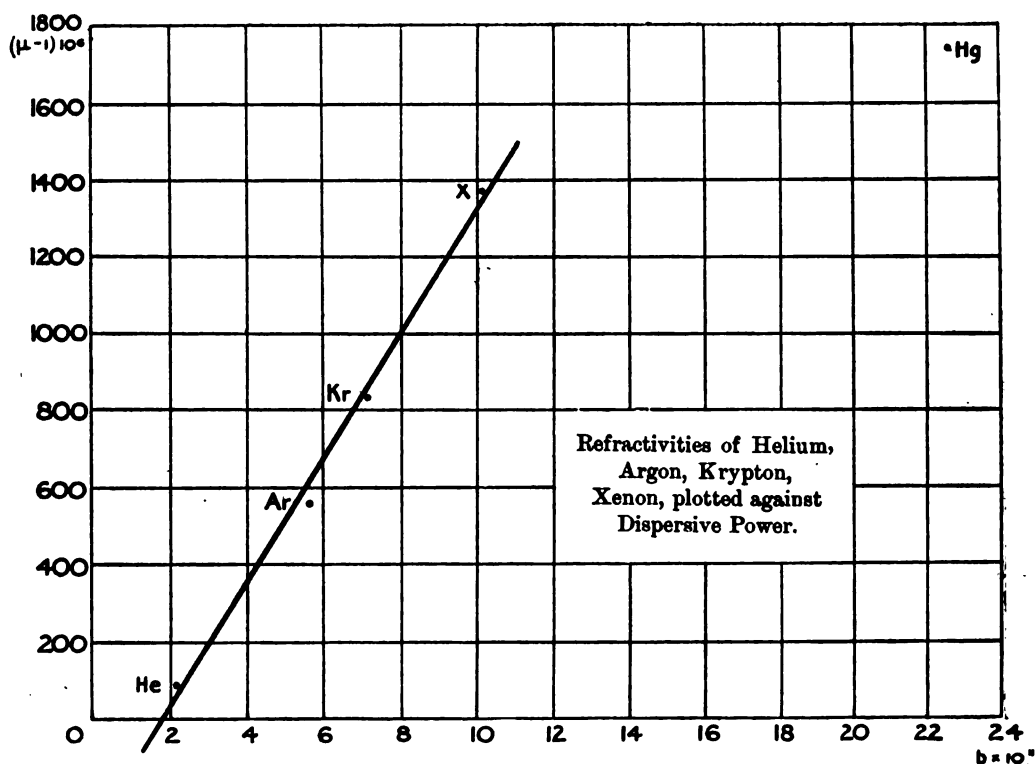
	$10^6 a/b$ .
Helium .....	31.62
Argon .....	99.72
Krypton .....	120.2
Xenon .....	134.5

Another relation between the refraction and dispersion can, however, be deduced. The accompanying diagram shows the values of  $b$  plotted against the refractivities for infinite wave-lengths given in Table IV.

A very good straight line can be drawn through the points representing helium, krypton, and xenon, and argon is not far off. If, instead of Burton's value for  $b$  for helium, we take Cuthbertson and Metcalfe's (2.4) the position of argon is improved. Burton states that his argon was prepared by Sir William Ramsay and obtained from Messrs. Tyrer and Co. He does not give its density. If it contained any nitrogen this would account for the large value of  $b$ , while the value of  $a$  would scarcely be affected. Considering

\* Mascart's value is 4.3; from Ketteler's measurements we have 6.69, from Lorenz 7.55, from Perreau 7.54, from Scheel 7.52.





The dots for X, Kr, and He should be closer to the line.

that, even for air, the values of  $b$  have varied so widely as from 5.8 (Mascart) to 5.2 (Kayser and Runge), it may fairly be said that within the limits of experimental error  $b$ , in the inert gases, is a linear function of the refractivity for infinite wave-lengths.

It is unfortunate that, at present, we are unable to compare with these results the dispersions of any other series of more than two elements. The dispersions of selenium and tellurium and of arsenic have been roughly measured, but not with sufficient accuracy to justify their use.\* But in the lighter members of the series to which they respectively belong the dispersions have been observed with somewhat greater accuracy, though the experimental results still leave much to be desired.†

The numbers found for nitrogen (Scheel) are

$$\mu - 1 = 0.00029061 \left( 1 + \frac{7.70}{\lambda^2 10^{11}} \right),$$

\* Cuthbertson and Metcalfe, 'Phil. Trans.,' A, vol. 207, p. 135.

† Cuthbertson and Metcalfe, "Dispersion of Gaseous Mercury, Sulphur, Phosphorus, and Helium," 'Roy. Soc. Proc.,' A, vol. 80, 1908.

and for phosphorus (Cuthbertson and Metcalfe)

$$\mu - 1 = 0.001162 \left( 1 + \frac{15.3}{\lambda^2 10^{11}} \right).$$

Similarly, the figures for oxygen (Mascart) are

$$\mu - 1 = 0.0002663 \left( 1 + \frac{5.07}{\lambda^2 10^{11}} \right),$$

and for sulphur (Cuthbertson and Metcalfe)

$$\mu - 1 = 0.0010457 \left( 1 + \frac{21.25}{\lambda^2 10^{11}} \right).$$

If we assume that in each group  $b = p + qa$ , where  $p$  and  $q$  are constants for the group, the values of  $p$  and  $q$  calculated from these figures are :—

	$p.$	$q.$
Inert gases (calculated from Kr and X) .....	$\frac{2.07}{10^{11}}$	$\frac{0.615}{10^7}$
Oxygen and sulphur .....	$\frac{-0.45}{10^{11}}$	$\frac{2.075}{10^7}$
Nitrogen and phosphorus.....	$\frac{5.15}{10^{11}}$	$\frac{0.875}{10^7}$

These numbers do not show any obvious relation, and more work is required before the law can be traced further. Thus, for example, the value of  $b$  for air ( $5.67/10^{11}$ ) cannot be deduced from the values for nitrogen; ( $b = 7.7/10^{11}$ ) and oxygen ( $b = 5.07/10^{11}$ ) here adopted from observers of high reputation. Mascart found for nitrogen the values 5.2, 7.6, and 7.3 in different parts of the spectrum, and pointed out that his values of  $b$  for nitrogen and oxygen could not be reconciled with his value for air, and that more accurate determinations were required.

It should, however, be remarked that, though the values of  $b$  for helium, krypton, and xenon obtained by us were calculated with reference to air, the linear relation which we find would not be affected by any change in the number adopted for the dispersion of air, which would increase or diminish all alike. A large error would affect their relation to Mr. Burton's values; but a large error is not to be feared.

In the diagram, the position of mercury is indicated, and it is plain that though it resembles the inert gases in being monatomic in the gaseous state, it does not fall into line with them in regard to the relation between refractive and dispersive power.

It remains to consider the physical meaning of the law deduced from our experiments. On comparing Cauchy's formula  $\mu - 1 = a(1 + b/\lambda^2)$  with the theoretical expression

$$\mu - 1 = \Sigma C/(n_0^2 - n^2),$$

and making the assumption that the latter has only one term, for which  $n_0^2$  is large compared with  $n^2$ , we have

$$a = C/n_0^2, \quad b = \lambda_0^2.$$

If  $b = p + qa$  for all the inert gases it would follow that the square of the wave-length of the free vibration dominating the dispersion is equal to a constant plus a term proportional to the refractivity for infinite wave-length.

We have great pleasure in expressing our thanks to Sir William Ramsay and Prof. R. B. Moore for the loan of the gases; to Prof. Trouton, Prof. Porter, and the staff of the Physical Laboratory of University College, London, for much assistance and advice; and to the Royal Society for a grant in aid of these experiments.

### *Note on Tidal Bores.*

By LORD RAYLEIGH, O.M., Pres. R.S.

(Received October 3,—Read November 5, 1908.)

It was shown long ago by Airy that when waves advance over shallow water of depth originally uniform, the crests tend to gain upon the hollows,\* so that the anterior slopes become steeper and steeper. Ultimately, if the conditions are favourable, there formed what is be may called a *bore*. Ordinary breakers upon a shelving beach are of this character, but the name is usually reserved for tidal bores advancing up rivers or estuaries. Interesting descriptions of some of these are given in Sir G. Darwin's 'Tides' (Murray, 1898).

Although the real bore advances up the channel, we may for theoretical purposes "reduce it to rest" by superposing an equal and opposite motion upon the whole water system. We have then merely to investigate the transition from a relatively rapid and shallow stream of depth  $l$  and velocity  $u$  to a deeper and slower stream of depth  $l'$  and velocity  $u'$  (fig. 1). The

FIG. 1.



\* See also 'Scientific Papers,' vol. 1, p. 253, 1899.

places where these velocities and depths are reckoned are supposed to be situated on the two sides of the bore and at such distances from it that the motions are there sensibly uniform. The problem being taken as in two dimensions, two relations may at once be formulated connecting the depths and velocities. By conservation of matter ("continuity") we have

$$lu = l'u'. \quad (1)$$

And since the mean pressures at the two sections are  $\frac{1}{2}gl$ ,  $\frac{1}{2}gl'$ , the equation of momentum is

$$lu(u-u') = \frac{1}{2}g(l'^2 - l^2); \quad (2)$$

$$\text{whence} \quad u^2 = \frac{1}{2}g(l+l') \cdot l'/l, \quad u'^2 = \frac{1}{2}g(l+l') \cdot l/l'. \quad (3)$$

The loss of energy per unit time at the bore is thus

$$lu(\frac{1}{2}u^2 + \frac{1}{2}gl) - l'u(\frac{1}{2}u'^2 + \frac{1}{2}gl') = lu \cdot g(l'-l) \frac{l^2 + l'^2}{4ll'}. \quad (4)$$

That there should be a loss of energy constitutes no difficulty, at least in the presence of viscosity; but the impossibility of a gain of energy shows that the motions here contemplated cannot be reversed.

In order to recur to the natural condition of things where the shallow water is at rest, we have to superpose the velocity  $u$  taken negatively upon the above motion. The velocity of the bore is then  $u$  and that of the stream above the bore  $u - u'$ . If  $l$  is relatively small,  $u$  is much greater than  $u'$ .

The reasoning just used is very similar to that applied by Stokes\* and by Riemann† to sound waves of expansion moving in one dimension. The matter is discussed in 'Theory of Sound,' § 253, where it is shown that the discontinuous solution, obtained from the principles of conservation of mass and momentum, violates the condition of energy. When this was pointed out to Stokes by Kelvin and later by myself,‡ he abandoned his solution, which is, however, maintained by a competent German authority.§ It is clear, at least, that when the motion is such as to involve a gain of energy, the solution cannot be admitted. The opposite case stands upon a different footing, and we may, perhaps, imagine the redundant mechanical energy to be got rid of somehow at the surface of discontinuity. Even then we should have to face the complication entailed by the development of heat. In the present case of liquid, the heat is of little consequence, and since the motion is not entirely in one dimension, we escape the necessity of dealing with a single plane of discontinuity.

\* 'Phil. Mag.,' vol. 33, p. 349, 1848.

† 'Göttingen Abh.,' vol. 8, 1860.

‡ Stokes, 'Math. and Phys. Papers,' vol. 2, p. 55.

§ Private correspondence.

*On a Method of Comparing Mutual Inductance and Resistance  
by the Help of Two-phase Alternating Currents.*

By ALBERT CAMPBELL, B.A.

(Communicated by R. T. Glazebrook, F.R.S. Received September 22,—  
Read November 5, 1908.)

(From the National Physical Laboratory.)

(1) *Introductory.*

A standard mutual inductance, after the design recently described by the writer,\* has now been constructed at the National Physical Laboratory. As the details of its construction will be published later, it is sufficient here to mention that its value calculated from the dimensions is 10·0178 millihenries. It forms an extremely accurate standard, against which both mutual and self inductances can be readily tested.† In addition to this, it affords a means of obtaining values of resistance coils in absolute measure, and thus evaluating the ohm. This can be done in an indirect way by finding the capacity of a condenser in terms of resistance and time by Maxwell's Commutator Method, and in terms of resistance and mutual inductance by Heydweiller's modification of Carey Foster's method. The comparison of resistance with mutual inductance can, however, be made far more simply and directly by the use of two-phase alternating currents in the method which I proceed to describe. I shall first take the ideal simple case, and afterwards notice some of the difficulties that may arise in practice.

(2) *Theory of the Method.*

In fig. 1 let  $M$  be the mutual inductance (a small fraction of it being adjustable) and  $R$  the resistance; and let  $A \cos pt$  and  $B \sin pt$  be currents in quadrature, *e.g.*, from a two-phase alternator or a phase-splitting device. Let  $G$  be a vibration galvanometer tuned to frequency  $n$ , where  $p = 2\pi n$ .

When the galvanometer shows no deflection, the electromotive force introduced into its circuit is zero at every instant, and hence

$$\frac{d}{dt}(MA \cos pt) + RB \sin pt = 0,$$

so that

$$R = \frac{A}{B} \cdot pM. \quad (1)$$

\* 'Roy. Soc. Proc.,' p. 428, June 5, 1907.

† See 'Phil. Mag.,' January, 1908, p. 155.

This condition gives a direct comparison between  $R$  and  $M$ , when  $p$  and  $A/B$  are known. By observing the speed of the alternator,  $p$  is found; while the ratio of  $A$  to  $B$  is obtained by means of the electrostatic voltmeter  $V$ , which is put alternately across the equal resistances  $r_1$  and  $r_2$ , or by a differential electro-dynamometer. In practice  $A$  is made very nearly equal to  $B$ .

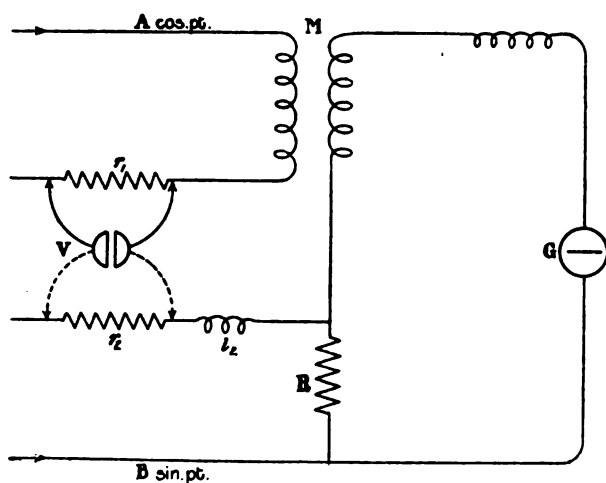


FIG. 1.

The condition of balance is arrived at by altering  $R$ ,  $M$ , or  $p$  until the galvanometer deflection becomes zero, accurate quadrature being maintained by adjusting the self inductance  $l_2$ . For example, if  $A/B = 1$ , for  $M = 10$  millihenries and  $R = 5$  ohms, the necessary frequency is about 80 cycles per second.

The chief difficulties at first sight would be in obtaining alternating current of absolutely pure sine wave-form; but the necessity for this is obviated by the use of the vibration galvanometer tuned to resonance with the fundamental in the wave-form, and thus ignoring the harmonics in comparison with the fundamentals  $A_1$  and  $B_1$ . This is found to be the case experimentally, for a sharply defined balance was obtained when a suitable alternator was used; and the mathematical investigation of the more general case substantiated this result. If necessary, the harmonics may be still further obliterated by electrical tuning with inductance and capacity in the galvanometer circuit. The effects of a small amount of self inductance in the resistance  $R$  and of distributed capacity in the secondary coil have been theoretically investigated; it has been found that the former is practically negligible, and that, if the latter is not quite negligible, the proper correction can easily be found.

*(3) Experimental Working of the Method.*

A few preliminary experiments have been made to test the working of the method. The measurement of  $A_1/B_1$  was made with a long scale electrostatic voltmeter which gave about 2 mm. for a difference of 1 in 10,000. Higher accuracy could no doubt be obtained by using an electro-dynamometer with two dynamically coupled moving coils; this would allow an accurate measurement of  $A_1 - B_1$  to be made. Errors would be eliminated by interchanging the two circuits of the instrument and taking the mean result. In the experiments already made, the frequency was held steady at a value approximately correct, and  $M$  was varied by the addition of a small accurately calibrated variable mutual inductance with a range of two or three thousandths of  $M$ .

The results obtained have been encouraging and appear to indicate that the method is susceptible of high accuracy. It may be of interest to mention that determinations obtained with an inductor alternator of extremely irregular wave-form showed errors of only 3 per cent.; while with a Siemens sine-wave alternator the divergence from the nominal values was within the limits of experimental error, which were of the order of 1 in 1000. This last is only the result of a preliminary trial; in the ultimate experiments the accuracy will be of a much higher order. —

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*The Occlusion of the Residual Gas and the Fluorescence of the  
Glass Walls of Crookes Tubes.*

By ALAN A. CAMPBELL SWINTON.

(Communicated by Sir William Crookes, F.R.S. Received October 5,—  
Read November 12, 1908.)

In a previous paper on the first part of this subject,\* the writer has described experiments indicating that the occlusion of the gas is due, at any rate in some instances, to the gas being mechanically driven into the glass, in which it forms bubbles on the glass being heated strongly.

Since this paper was published, several comments on the writer's conclusions have appeared, and these have led to the writer making further experimental investigations which it is one of the purposes of this paper to describe.

In a lecture on March 16, 1907, at the Royal Institution,† Prof. J. J. Thomson suggested an explanation of the considerable depth from the inner surface of the glass at which the bubbles occur. This depth, as measured by the writer, amounts in some cases to more than one-tenth of a millimetre, which is a considerably greater distance than cathode rays are found to penetrate through aluminium. Prof. J. J. Thomson pointed out that both glass and silica have been shown to be permeable to hydrogen and helium at high temperatures, so that the effect in question might arise from the cathode ray bombardment raising the temperature of the surface of the glass sufficiently to permit of these gases penetrating by ordinary diffusion.

Again, in a paper entitled "The Formation of Gas Bubbles in the Walls of Heated Discharge Tubes," read before the German Physical Society on June 28, 1907,‡ Mr. Robert Pohl disputes the contention of the writer that the gas is driven mechanically into the glass, and maintains that the formation of the bubbles is entirely due to the presence of films of aluminium disintegrated from the electrodes and to chemical action connected with the oxidation of this aluminium when the glass is heated in a flame.

Finally, Mr. Frederick Soddy and Mr. Thomas D. Mackenzie, in their paper on "The Electric Discharge in Monatomic Gases," read before the Royal Society, November 7, 1907,§ from experiments made on argon, neon, and

\* "The Occlusion of the Residual Gas by the Glass Walls of Vacuum Tubes," 'Roy. Soc. Proc.,' A, vol. 79, pp. 134—137.

† See 'Engineering,' March 22, 1907, p. 387.

‡ 'Berichte der Deutschen Physikalischen Gesellschaft,' pp. 306—314.

§ 'Roy. Soc. Proc.,' A, vol. 80, pp. 92—109.



helium spectrum tubes, seem to have come to the conclusion that the gas which causes the bubbles is not the residual gas in the tube, but is gas generated by chemical decomposition of the glass under the influence of local heating produced by the discharge, which heating in the case of their particular tubes was probably very considerable.

First of all, to deal with Mr. Robert Pohl's conclusions, as the writer's previous experiments did not at all bear these out, it was decided to make a

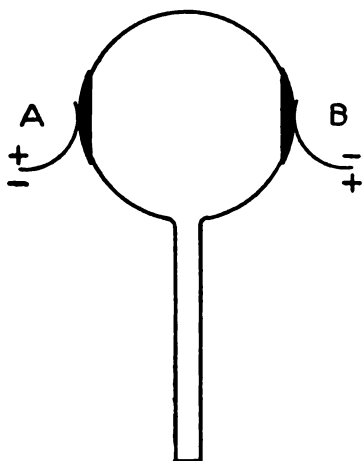


FIG. 1.

crucial experiment in which there would be no possibility of the presence of any aluminium within the tube. For this purpose a vacuum tube was constructed as shown in fig. 1, the electrodes consisting of two caps of tinfoil, A and B, pasted on the outside of the tube. The tube was pumped up to a vacuum at which it gave green fluorescence. Alternating current at about 7000 volts was employed, this giving a current of 1 to 2 milliamperes, which was found to be as much as the tube would stand without getting warm.

After sparking for  $7\frac{1}{2}$  hours the tube was broken up, when it was found that on portions of the glass being strongly heated in a blowpipe flame they immediately became filled with large numbers of very small bubbles. These bubbles were on the average about half the diameter of those observed by the writer in his previous experiments with tubes containing internal electrodes, and were also much nearer the surface of the glass, the depth being only about 0.025 mm. as against the 0.122 mm. measured in the case of the previous experiments. These variations are no doubt due to the fact that with tubes with external electrodes only very weak electrical discharges can be obtained, and the bombardment consequently is much less violent. These experiments, which were repeated several times with different tubes, always with similar results, appear entirely to dispose of Mr. Pohl's contention that the presence of a film of aluminium, or for that matter of any other metal, on the inside surface of the tube is in any way requisite for the production of the bubbles.

Furthermore, it was found that boiling the glass of these tubes with external electrodes in strong nitric acid, prior to heating in the flame, did not prevent the formation of the bubbles except in one case in which, after sparking for a number of hours, the interior surface of the tube was found to

be covered with a brown film which was dissolved away by the boiling nitric acid, after which process no bubbles could be obtained in the glass. The writer is indebted to Mr. J. Thomas, of Faraday House, for making an analysis of this brown deposit, from which it appears that it consisted of carbon, due, as the writer has since ascertained, to volatile portions of the grease used in a stopcock on the pipe employed for exhausting the tube. It would appear, therefore, that when there is a sufficient deposit of this nature the occlusion takes place in the deposit and not in the glass as it does when no deposit is present.

Next, experiments were made with a view to ascertaining whether under the bombardment the gas is driven into the glass to as great a depth as that at which the bubbles appear on subsequent heating.

In all cases, whether internal or external electrodes were employed, it was found that grinding away the interior surface of the glass to a sufficient extent prevented any formation of bubbles on subsequent heating, and by just grinding to the extent necessary for this purpose and measuring the thickness of the glass before and after grinding, it was possible to estimate the distance which the gas had travelled into the glass under the bombardment, prior to the heating of the glass in the flame.

In specimens of glass from different tubes this distance was found to vary from 0.0025 mm. with external electrodes to as much as 0.015 mm. with internal electrodes, the differences being no doubt due to the varying velocities of the cathode rays, but in all cases this distance was found to be considerably less—usually in the ratio of about 1 to 10—than the distances between the surface of the glass and the centres of the bubbles produced by heating in the flame. From this it would appear that the gas travels considerably further into the glass when the latter is strongly heated.

As difficulties were met with in making accurate measurements owing to the curvature and irregular thickness of the glass of the tubes, in some of the experiments a piece of flat microscope cover glass, laid inside the tube in a position where the bombardment would reach it, was employed instead of the walls of the tube itself. As regards the penetration of the gas and the production of bubbles, this cover glass was found to behave exactly like the glass of the tube. It was also found that the depth of the bubbles in the glass could be very easily determined by examining the glass edgewise in a microscope. Observations made in this way showed that the bubbles, though in one layer, are usually at by no means a uniform depth.

Experiments were also made to ascertain what is the maximum distance that cathode rays will penetrate aluminium. For this purpose a small fluorescent screen of Willemite was placed behind a patchwork screen of

aluminium foil, the four patches into which the latter was divided being composed of two, three, four, and five thicknesses respectively of aluminium 0.0028 mm. in thickness. The whole was placed in a tube opposite a flat cathode, so that the rays could only reach the Willemite after passing through the aluminium. With this arrangement it was found that the five thicknesses of foil gave about the limit through which the cathode rays would pass, at any rate sufficiently to cause fluorescence, the amount of fluorescence obtained through the five thicknesses being exceedingly feeble, and only visible at all with cathode rays of a very active description.

From this it appears that the maximum thickness of aluminium through which cathode rays can ordinarily be made to pass in any quantity is about 0.014 mm., which, as the density of aluminium is 2.7 and that of glass about 2.47, agrees very fairly closely with the figure of 0.015 mm., which, as mentioned above, was found to be the maximum distance that the gas penetrated into the glass before heating sufficiently to form bubbles on subsequent heating in the flame.

It should be mentioned that in the experiments already alluded to on the tubes with external electrodes, the electric discharges passing through the tubes were so weak that the heating of the glass was very slight, the temperature of no portion of the exterior of the tubes exceeding that of the surrounding atmosphere by more than a very few degrees. Even after allowing for the fact that the instantaneous temperature of the interior of the tubes during each discharge would be higher than the mean temperature of the exterior, it does not seem possible that the temperature can have been sufficiently raised either to allow of the gas passing into the glass by ordinary diffusion, as suggested by Prof. J. J. Thomson, or to have caused the gas to be evolved inside the glass by chemical decomposition due to heat as put forward by Mr. Soddy and Mr. Mackenzie.

Furthermore, neither of these explanations seems really necessary, for, as has been shown, the gas in the first instance travels into the glass only about the same distance that cathode rays can be made to pass through aluminium, and it is therefore reasonable to suppose that the gas may be driven in mechanically. Diffusion, however, probably plays an important part in the final result, taking place at the later stage when the glass is softened in the flame. Under its influence, and also, perhaps, under that of surface tension, the gas then travels much further into the glass and forms bubbles at the moment of solidification, in much the same way that air dissolved in water forms bubbles when the water is frozen into ice.

No doubt where there is considerable deposit on the glass of aluminium from the electrodes, of platinum or of other material employed from the anti-

cathode, or of carbon as above instanced, the occlusion may take place largely in such deposit, but otherwise the above experiments seem to bear out the writer's original conclusion that the occlusion is due to the gas being mechanically driven into the glass itself.

Experiments were also made in order to discover whether the penetration of the gas into the glass has any bearing on the fatigue of the latter in respect to fluorescence, discovered by Sir William Crookes nearly thirty years ago.\*

In many cases this fatigue, according to the writer's observations, is due to deposits of aluminium or other electrode matter or of carbon on the glass, barely noticeable deposits having a marked effect in this respect. In other cases, however, fatigue shows itself where the most careful examination can find no evidence of such deposits, or after they have been removed, and where the cause of the fatigue must therefore be sought elsewhere.

In order to investigate the matter, a strip of glass was mounted in a tube opposite to a flat aluminium cathode, with a screen consisting of a strip of sheet iron considerably narrower than the strip of glass placed between the cathode and the glass, so as to shield a central zone of the latter from the bombardment. The iron screen was hinged at the end where it was supported, so that by means of a magnet it could be moved out of the way so as to allow the whole of the glass strip to be uniformly bombarded when required.

The tube was exhausted to a state in which the glass fluoresced brightly, and with the iron screen in position to shield part of the glass strip, the latter was subjected to vigorous bombardment for some seven hours. At the end of this period the bombarded glass showed very considerable fatigue, and when the iron screen was moved so as to allow the cathode rays to strike the whole surface, fluoresced much less brightly than the portion that had been shielded. Furthermore, the fatigue of the glass was found to be permanent to the extent that it had not perceptibly diminished after a rest of some sixteen hours.

The glass strip was next removed from the tube, and after its thickness had been carefully measured with a microscope a layer of wedge section of part of the bombarded surface was removed by grinding. On replacing the strip in the tube, and again subjecting the whole of it to bombardment, it was found that part of the strip where most glass had been ground off now showed no signs of fatigue, and fluoresced as brightly as the portion that had been screened from the initial bombardment, while those parts off which only little glass had been ground, or none ground off at all, still

\* 'Phil. Trans.,' 1879, part 2, p. 645.

showed the fatigue, there being a well-defined line of demarcation between the fatigued and non-fatigued portions. On again removing the glass from the tube and measuring in the microscope its thickness at this line of demarcation, and comparing the figure with that of the original thickness of the glass, it was found that the thickness of the glass that had been removed at this point was 0.017 mm., this being the amount of glass that had to be ground off in order to do away with the fatigue. The experiment was repeated several times with both longer and shorter periods of bombardment, but always with similar results, the measurements varying but little. Also it was found to make little difference whether a separate piece of glass mounted in the tube, or a bombarded portion of the walls of the tube itself, were employed for the experiment. As will be observed, the figure of 0.017 mm. approximates very closely to the 0.015 mm., which, in tubes with internal electrodes, was the distance that the gas was found to be driven into the glass by the bombardment in quantities sufficient to form bubbles on subsequent heating.

Furthermore, experiments showed that glass which had been well bombarded by cathode rays so as to be greatly fatigued, and off a portion of which a layer had been ground of just sufficient thickness to restore the fluorescence of that part to the original brilliancy when tested under further bombardment, evolved bubbles under subsequent heating in a blowpipe flame only in those parts which had not been ground down sufficiently to remove the fatigue, the line of demarcation between those portions of the glass that gave and did not give bubbles on heating being very nearly though not quite identical with that between the portions that did and did not show fatigue. In each case the want of identity between these lines of demarcation showed that a slightly greater thickness of glass must be removed to do away with fatigue than is sufficient to prevent the formation of bubbles. This seems natural, as fluorescence under cathode ray bombardment is a surface effect, and it does not therefore signify so far as it is concerned whether the layer permeated by the gas is thick or thin; whereas for bubbles to be formed on heating, the gas must probably be located in the glass at not less than some definite minimum mean depth, at less than which the gas merely escapes when the glass is heated.

From the above it would appear, in some cases at all events, that the fatigue of the glass is intimately connected with, and is perhaps the direct result of, the penetration of the gas, for, as should be pointed out, the thickness of the layer of fatigued glass is quite considerable, and much greater than that of any surface deposits of carbon or of aluminium which, as already mentioned, have also the effect of diminishing the brightness of

the fluorescence, and are, partially at any rate, in some cases the cause of fatigue.

The further suggestion that the fatigue may be due to the actual presence of the gas in the glass may help to explain the permanent nature of the fatigue where there is no carbon, aluminium or other deposit, for, as mentioned in his previous paper referred to above, the writer obtained bubbles in portions of the walls of a tube due to gas which had been imprisoned in the glass for some nine years. That the fatigue is very permanent is further borne out by the fact that the writer finds that the glass of a Crookes tube containing a hinged aluminium cross, of the usual description for showing this fatigue phenomenon, which has been lying unused since the year 1898, is still sufficiently fatigued by the bombardment it received ten years ago to show quite distinctly the usual appearance of a bright fluorescent image of the cross on a less bright background when the glass is uniformly bombarded, though no signs of any discoloration due to deposition of carbon or of aluminium or of other effect on the glass are visible by ordinary light. Though some portion of the fatigue effect is permanent, the remainder, which as a rule is the larger part, is but temporary. This may be due to the gradual escape of such portion of the gas as has been driven into the glass only such a very short distance that the latter is unable permanently to retain it.

The writer is again indebted to Mr. J. C. M. Stanton and Mr. R. C. Pierce for their assistance in carrying out the experiments.

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*Note on Two recently compiled Calendars of Papers of the Period  
1606—1806 in the Archives of the Royal Society.*

By A. H. CHURCH, D.Sc., F.R.S.

(Received October 26,—Read November 5, 1908.)

The second section of Chapter XVI of the Statutes of the Royal Society commences with these words: "A catalogue of the manuscripts in the archives shall be available for reference at the rooms of the Society." Now a catalogue assigning a single number and title to a whole volume or collection of more or less independent documents does not afford much help to the inquirer. However, one detailed catalogue, dealing, item by item, with a large part of the correspondence of the Society, down to the year 1740, was compiled by Mr. W. E. Shuckard, the Librarian, and published in 1840. The arrangement adopted in cataloguing the documents preserved in the 48 "Letter-Books" of this series, was alphabetical for authors, and chronological in the sequence of the contributions of each writer. Parallel with these "Letter-Books," there exists a set of guard-books, 39 in number, filled mainly with early classified MS. papers of the period 1606—1741. These documents, about 2500 in number, the production of some 800 authors, were catalogued in 1907, a manuscript Calendar being compiled, together with an Introduction and *Index Nominum*, both since printed. The titles and numbers attached to the several guard-books of this series are here given: it should be noted that the documents had been arranged mainly in accordance with their subjects, but in a few instances by authorship. There has been given to this set the designation—

CLASSIFIED PAPERS.

VOLUME

- i. Arithmetick, Algebra, Geometry, Trigonometry.
- ii. Surveying, Opticks, Perspective, Sculpture, Painting, Musick, Mechanicks.
- iii (1) and iii (2). Mechanicks, Trades.
- iv (1) and iv (2). Physiology, Meteorology, Pneumatics.
- v. Journals of the Weather.
- vi. Statics, Hydrostatics, Hydraulicks, Hydrology.
- vii (1) and vii (2). Architecture, Shipbuilding, Geography, Navigation, Voyages, Travels.
- viii (1) and viii (2). Astronomy.
- ix (1) and ix (2). Mineralogy, Magneticks.
- x (1), x (2) and x (3). Botany and Agriculture.
- xi (1) and xi (2). Pharmacy and Chymistry.
- xii (1) and xii (2). Anatomy and Surgery.
- xiii. Monsters ; Longevity.

**VOLUME**

- xiv (1) and xiv (2). Physick.
- xv (1) and xv (2). Zoology.
- xvi. Grammar, Chronology, History, and Antiquities.
- xvii. Miscellaneous Papers.
- xviii (1) and xviii (2). Experiments of Papin, Hawksbee, and Desaguliers.
- xix. Inquiries and Answers.
- xx. Dr. Hook's Papers.
- xxi. Halley's Papers.
- xxii (1) and xxii (2). Accounts of Books.
- xxiii (1) and xxiii (2). Inoculations.
- xxiv. Papers by Collins, Oldenburg and Hook.
- xxv. Political: Trade.

Although some notion of the character and range of these "Classified Papers" may be formed from the titles given to the several books, yet a reference to the MS. Calendar will be required should exact details of any particular paper be wanted. Here the printed Index of Authors' names will be found useful. Still there are many papers which, being anonymous, cannot be reached in this way. In this connection may be mentioned two long lists of manuscripts in various libraries; these lists are Nos. 32 and 33 in vol. xvii. Of authors' names in the Index which afford no clue to the subjects of their papers are those of a number of persons concerned in the farming of sea-coals and the trade therein, both at Newcastle and in Scotland. These papers are Nos. 29 to 55 in vol. xxv, and belong to the period 1610—1633. They, and many others dated long before the foundation of the Royal Society, scarcely belong to the Archives, but are interesting in themselves and afford material useful in tracing the antecedents, the scope, and the development of the Society.

It is scarcely necessary to state that the majority of the documents preserved in this set of guard-books consists of papers communicated to the Society. Of these a good many were never published in the 'Philosophical Transactions.' In the printed pamphlet which was distributed last year to the Fellows, some further particulars concerning the Classified Papers are given.

Attention may now be drawn to a third set of guard-books containing both letters and papers, and forming a continuation of both the earlier sets, that is, of the "Letter-Books" and of the "Classified Papers." The 127 volumes of this third set begin in the year 1741 and close in 1806. Their contents are arranged chronologically, but there are a few gaps in the sequence, while some documents have been misplaced. In the earlier papers the form of a letter was generally adopted—even at the end of the period it was not unusual.



While the bulk of these guard-books is made up of papers and memoirs, yet letters to and from the officers of the Society, as well as reports from special committees, are not infrequent. Some of the acknowledgments sent by foreign members on election into the body are fortunately preserved. Among these may be cited the letters of Pierre de Vigny, Carolus Linnæus, the Abbé Jean Jacques Barthélemy, le Comte de Saluces, Jean Bernard, M.D., and Michel Adanson; such letters, though read at the meetings, were not printed. Indeed the student of the documents, over 3650 in number, preserved in this long series of guard-books, cannot but feel a special interest in those letters and papers which did *not* appear in the 'Philosophical Transactions.' Some of these have been noted in the printed pamphlet which has been prepared to accompany and explain the MS. Calendar of this collection, while four unpublished letters, one each from Benjamin Franklin, Carolus Linnæus, Captain James Cook, and John Hunter, have been printed in full, as typical examples.

Most of these "Letters and Papers," being signed holographs mainly of notable persons, afford abundant material for the study of handwriting. But the collection is much more than a collection of autographs, for it contains the original announcements of most of the great discoveries in "natural knowledge" by which the latter part of the eighteenth century was marked in Great Britain, nor are noteworthy contributions from foreign philosophers wanting. Many original illustrations, including some excellent water-colour drawings (such as those by the Rev. John Lightfoot and Edward Edwards, A.R.A.), are here preserved. As a matter of minor interest, mention may be made of the fine armorial seals attached to a number of the letters; these are noted in the MS. Calendar.

Throughout these guard-books occur the original MSS. of many of the Croonian and Bakerian Lectures. Unpublished discourses of the former series include some by James Douglas, John Hunter, Samuel Foart Simmons, Edward Whitaker Grey, Sir Gilbert Blane, Sir Wm. Blizard, Mathew Baillie, Sir Everard Home, John Abernethy, and John Pearson. There are unprinted Bakerian Lectures by Peter Woulfe, Tiberius Cavallo, and Samuel Vince.

The compiler of the MS. Calendar, and of the printed pamphlet already mentioned, has met with many difficulties in his task. The names of authors are not always legible in the original manuscripts; frequently, Christian names being omitted, they had to be sought elsewhere. Moreover, in a few cases where names were apparently identical, there might be indications that they belonged to two individuals, not one; mistakes in the opposite sense may also have occurred. But the value of an *Index Nominum* warranted the

devotion of much time and trouble to rendering it more useful than it could have proved had no errors been corrected and no deficiencies supplied from sources outside the "Letters and Papers" themselves.

The construction and the mode of using the printed Index may now be briefly described. The 127 guard-books were taken in groups of ten, or Decades, a fresh numeration of the documents being commenced with each Decade. Thus, Decade I includes guard-books 1 to 10A; Decade II, 10B to 20; Decade III, 21 to 30, and Decade XII the guard-books 111 to 119. As, however, there are irregularities in the original numbering of the books, some of the Decades have to comprise supplementary volumes and appendices. Two figures are attached to each document in the Index; the first, a Roman numeral, refers to the Decade, the second, an Arabic numeral, points to the particular paper in that Decade. As an example, we turn to the Index, and find, under JENNER, EDWARD, M.D., the figures IX 37. On referring to the MS. Calendar, and to the section dealing with Decade IX, we read, under Dr. Jenner's name, that the document No. 37 is entitled "Of the Cuckoo"; that it is a signed holograph of 32 pages, dated: Berkley, Feb. 20, 1787. Further, we note that it is endorsed "cancelled at the desire of the Author, C. B., Sec. R.S." The paper itself will be found in one of the guard-books labelled "Decade IX, Nos. 23 to 49." There is no need to ascertain the old number attached to the guard-book in question (it is 82), as the new label on the volume gives all necessary information; a mark in blue pencil, on the first guard to which the document is pasted, indicates its number in the Decade.

#### LETTERS AND PAPERS.

The approximate dates covered by the several Decades, with the number of calendared documents in each Decade, are shown in this conspectus:—

Decades.	Dates.	Documents.
I. October	1741 to October	1746..... 480
II. December	1749 „ March	1755..... 586
III. March	1755 „ March	1760..... 426
IV. March	1760 „ November	1767..... 415
V. January	1768 „ December	1772..... 330
VI. November	1773 „ December	1777..... 260
VII. January	1778 „ June	1782..... 272
VIII. November	1782 „ June	1786..... 190
IX. June	1786 „ January	1792..... 221
X. February	1792 „ March	1796..... 150
XI. June	1796 „ December	1801..... 175
XII. December	1801 „ June	1806..... 146

It will be seen that there are now at the disposal of Fellows of the Society two newly-compiled Calendars of papers in the Archives, with corresponding

printed Indexes of some 2150 Authors. These cover a period of 200 years, deal with more than 6150 documents preserved in 166 guard-books, the contents of which were, until now, very little known, and, though accessible, were scarcely available for purposes of study.

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*The Charges on Ions in Gases, and the Effect of Water Vapour on the Motion of Negative Ions.*

By Prof. JOHN S. TOWNSEND, F.R.S.

(Received November 3,—Read November 12, 1908.)

1. In a paper published in the 'Proceedings of the Royal Society,' vol. 80, p. 207, January, 1908, a method was given for comparing the charges on ions in liquids and gases. The first set of experiments gave results in accordance with the theory, and it was found that the charge on a positive ion in a gas was double that of a negative ion, the latter being equal to the charge on a monovalent ion in a liquid electrolyte. The ratio of the charges obtained was  $2.4 \pm 1.23$ .

The ions were produced by secondary Röntgen rays emitted by a brass surface, and further experiments have shown that positive ions with double or single atomic\* charges may be produced, the number of either kind depending on the nature of the secondary rays, which is determined by the state of the metallic surface from which they originate.

In all cases the negative ions have a single atomic charge.

Another difference between the positive and negative ions has also been found. It will be seen from the experiments to be described that the motion of a negative ion in an electric field is influenced to a great extent by the presence of water vapour in very small quantities, there being no corresponding effect with positive ions.

2. In the first set of experiments that were made no particular attention was paid to the state of the surface at which the secondary rays were produced, and when the air-tight cover was taken off the apparatus it was found that this surface was very much tarnished. The surface was carefully cleaned with the intention of getting a sufficient number of ions generated in the gas

\* For simplicity the charge on a monatomic ion in a liquid electrolyte may be termed the atomic charge. Denoting its value in electrostatic units by  $e$ , then  $Ne = 1.225 \times 10^9$ ,  $N$  being the number of molecules in a cubic centimetre of a gas at 760 mm. pressure and temperature  $15^\circ \text{C}$ .



potential of the battery connected to the primary of the coil with which the Röntgen ray bulb was worked.

It would appear from this that positive ions with two atomic charges are produced by the more penetrating secondary radiation.

3. In order to explain the effect of slight traces of moisture on the motion of the negative ions, it is necessary to refer more particularly to the theory of the experiments. The accompanying figure shows the arrangement of the apparatus. The primary rays P enter the apparatus through an aluminium window in the brass cover (not shown in the figure), and passing through an annular opening in the thick upper plate, fall on the plate S.

Some of the ions generated by the secondary rays pass through the grating under the electric force, and then through the aperture A into the lower field. The stream of ions opens out, and the central portion falls on the disc D, and the rest on the ring C, the charges  $n_1$  and  $n_2$  received by each being measured accurately by a special form of induction balance. Intermediate between the ring with the aperture A and the ring  $R_0$  were a series of flat rings at equal distances apart, connected in series by high resistances so that when  $R_0$  is put to earth and the plate S was raised to a potential  $V_1$  there is a perfectly uniform field in the space below the grating G. (The disc D and plate C were cut from the same sheet of brass so that there should be no contact potential between them.)

In the first form of the apparatus the diaphragm was placed touching the grating just below it; it was afterwards placed at a centimetre below the grating, as it was considered that the uniformity of the lower field would be better secured by that arrangement. The advantage of this change was, however, very slight, as the same results were obtained with both forms of apparatus when the change in distance of the diaphragm from the lower plate was taken into consideration.

When a uniform stream is passing through the aperture A, the partial pressure  $p$  of the ions at any point in the field of uniform force  $Z$  is given by the equation

$$\frac{d^2p}{dx^2} + \frac{d^2p}{dy^2} + \frac{d^2p}{dz^2} = eZ \frac{dn}{dz}, \quad (1)$$

$e$  being the charge on an ion and  $n$  the number of ions per cubic centimetre. The kinetic energy acquired by an ion under the force  $Z$  along the free path  $l$  is proportional to  $Z.l$ , and when this energy is small compared with the energy of translation of a molecule of the surrounding gas, then the equation

$$p = \frac{\Pi}{N} \cdot n$$

holds for the ions, since the kinetic energy of translation of a given number of ions will then be equal to the energy of translation of an equal number of molecules. In equation (2),  $N$  is the number of molecules per cubic centimetre in a gas at atmospheric pressure  $\Pi$ , and at a temperature equal to that of the gas in the experiments.

Eliminating  $n$ , equation (1) becomes

$$\nabla^2 p = \frac{N \cdot e \cdot Z}{\Pi} \cdot \frac{dp}{dz}. \quad (3)$$

This equation can be easily solved, and the ratio  $R$  of the charge  $n_1$  received by the disc  $D$  to the whole charge  $n_1 + n_2$  may be found in terms of  $N \cdot e \cdot Z$ .

Thus

$$R = f(N \cdot e \cdot Z). \quad (4)$$

The function  $f$  is a somewhat complicated expression when expanded in a series of Bessel's functions, so that for purposes of reference it is convenient to represent it graphically. The continuous curve 1, fig. 2, represents the values of  $R$  corresponding to the force  $Z$  which is expressed in volts per centimetre,  $Ne$  being taken as  $1.225 \times 10^{10}$ . The curve corresponds to an apparatus in which the aperture  $A$  is 1.5 cm. in diameter and 7 cm. from the ring  $C$  and disc  $D$ .

In order to be certain that equation (2) is satisfied, it is necessary to make experiments and see (*a*) that  $R$  is independent of the pressure of the gas in the apparatus, and (*b*) that  $R$  varies with the force according to equation (4), when a definite value is assigned to  $Ne$ . The latter condition can be tested by means of the curve.

These two conditions (*a*) and (*b*) have been found to hold with various forces and pressures in all the experiments that have been made, except in the case of negative ions when the gas is very dry.

4. In order to obtain this effect, it is necessary to have the drying agent inside the cover of the apparatus or in vessels connected to the apparatus by short lengths of wide tubing. After the drying has been going on for three or four days, a decrease can be observed in the ratio  $R$  for negative ions with the higher forces and lower pressures of the gas. As the drying proceeds the effect becomes noticeable with the smaller forces and larger pressures.

The three dotted curves, fig. 2, represent the values of  $R$  obtained experimentally after the gas had been drying for several weeks, and no further changes were noticeable. The curves correspond to pressures 16.5, 11, and 5.5 mm. of the gas.

It is remarkable that the stream of ions coming through the aperture A opens out considerably when the pressure is lowered ( $R$  diminishes), also for the larger values of the forces the spreading of the stream is not much altered by changing the force ( $R$  nearly constant).

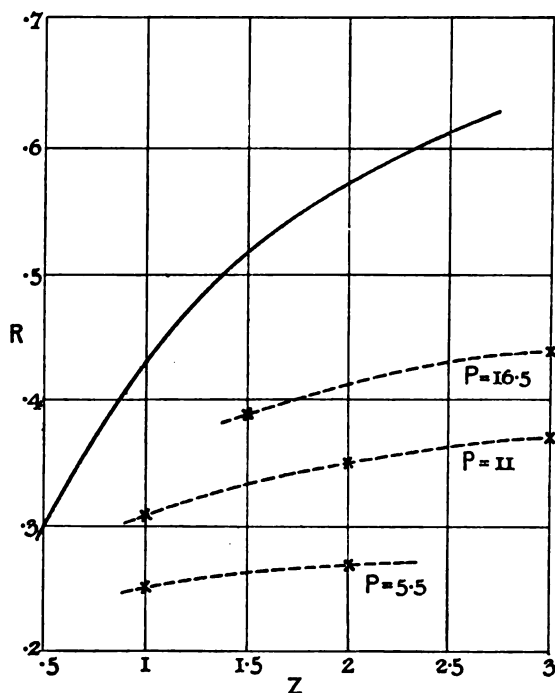


FIG. 2.

These results have been obtained with negative ions both when the surface S was polished and when there is a thin layer of vaseline on it. No corresponding effect has been observed with positive ions, for which the values of  $R$  continue to satisfy the conditions (a) and (b) when the gas is dry.

A small amount of water vapour may be easily admitted to the apparatus by connecting it for a few minutes with narrow tubing to an exhausted bulb containing a little water. The ratios  $R$  for negative ions then immediately return to their original values as given by the theoretical curve, and are independent of the pressure. Experiments of this kind have been made several times and always with the same result, so that there can be no doubt that the changes are due to the water vapour. An amount of water vapour having a partial pressure of less than  $1/10$  mm. is sufficient to produce the change, and further additions of vapour produce no effect on the value of  $R$ .

5. There is no noticeable change in the number of the ions produced by the rays when this small quantity of vapour is admitted, so that it is improbable that the process of ionisation of the molecules of the gas is in any way changed. The experiments cannot be satisfactorily explained by supposing the charge  $e$  to be variable and less than the atomic charge when the gas is dry, but it can easily be seen that an increase of the partial pressure of the ions due to the action of the force  $Z$  would produce results of the kind that have been observed, the charge on each negative ion being equal to the atomic charge. In all cases there must be a limit to the range of forces over which equation (2) will be satisfied. It has been shown\* that the negative ions produced by the rays from molecules of a gas are smaller than the positive ions, and therefore their free paths longer, so that it is to be expected that the limit would be reached with a smaller force for negative ions than for positive ions. The effects observed, however, are probably not due altogether to the difference in the free paths of the two kinds of ions, but may partly arise from the difference between their masses.

The velocity of translation of the ions increases under the electric force, and when collisions with molecules occur the ions do not in general lose all the energy they acquire but continue to move in all directions with increased energy after several collisions. The partial pressure of the ions therefore is in excess of that of an equal number of the surrounding molecules while the force is acting, but the difference would be quite inappreciable except when the force is large and the pressure small. The value of the force where this effect begins to be of importance could be found by these experiments, since the partial pressure  $p$  of a given number of ions  $n$  would exceed the value  $p = \Pi \cdot n/N$  by a factor which depends on the force, so that equation (4) would no longer hold.

When  $p$  is increased owing to the action of the force, an equation

$$p = k \frac{\Pi}{N} n, \quad (5)$$

must be used to determine  $n$  for substitution in equation (1), and the differential equation for determining  $p$  at any point in the field of uniform force  $Z$  becomes

$$\nabla^2 p = \frac{Ne}{\Pi} \frac{Z}{k} \frac{dp}{dz}, \quad (6)$$

where  $k$  is greater than unity, increasing with the electric force, and diminishing with increase of pressure of the surrounding gas, since an increase in the number of collisions with molecules diminishes the free

\* J. S. Townsend, 'Phil. Mag.,' June, 1902, p. 574.



paths and tends to equalise the energy of translation of the ions and the molecules. The definition of the quantity  $k$  is contained in equation (5), it represents the ratio of the partial pressure of the ions to that of an equal number of molecules of the surrounding gas.

The solution of equation (6) is of the same form as that of equation (3), since  $k$  does not vary from point to point in the gas, so that

$$R = f\left(N \cdot e \cdot \frac{Z}{k}\right). \quad (7)$$

The value  $R$  as given by this equation for a force  $Z$  is the same as the ratio  $R$  for a smaller force  $Z_1 (= Z/k)$  when the gas is slightly moist and  $k = 1$ .

There is one simple relation that should hold between the values of  $k$  for the different forces and pressures which may be tested by the experimental results. It is obvious that  $k$  must depend only on  $Z \cdot l$  or  $Z/P$ , since the free path  $l$  is inversely proportional to the pressure  $P$  of the gas, so that  $k$  must be a function of  $Z/P$ . The values of  $k$  corresponding to the different forces and pressures can be found from the experiments, and it may be seen that the condition  $k = \phi(Z/P)$  is satisfied.

If  $R$  be the ratio corresponding to the force  $Z$  for the dry gas, the force  $Z_1$  which would give the same ratio when  $k = 1$  may be found from the continuous curve, fig. 2, so that  $k = Z/Z_1$  is easily determined. The following table gives the values of  $k$  for the different forces  $Z$  and pressures  $P$  :—

$Z$ .....	1	1.5	1	2	3	1.5	3
$P$ .....	11.0	16.5	5.5	11	16.5	5.5	11
$k$ .....	1.85	1.83	2.86	2.90	2.85	3.75	4.00
$Z/P$ .....	0.091	0.091	0.182	0.182	0.182	0.273	0.273

Thus the experimental results obtained with variations of the force and pressure show that  $k$  does not alter when  $Z$  and  $P$  are changed in the same proportion, so that the above condition is satisfied.

The effects observed with negative ions in a dry gas may therefore be attributed to the increase of partial pressure which they can acquire when they are of small dimensions. Since the motion of the negative ions corresponds to that of particles of larger dimensions (*i.e.* positive ions), when water vapour is present it may be concluded that the water vapour even at a very low pressure tends to condense on the negative ions.

An effect of water vapour on the motion of negative ions was first observed

in the experiments on diffusion of ions in gases at atmospheric pressure.\* Prof. Zeleny† also, in his experiments on the velocity of ions under an electromotive force, observed a corresponding effect. The changes were produced by large pressures of water vapour, and were comparatively small. The effects of small traces of water vapour could not have been investigated by the methods employed in those experiments, as large volumes of gas were used. Possibly the motion of negative ions in gases at high pressures is not influenced by small traces of water vapour, but experiments on the velocity of ions under an electromotive force are being made to investigate the matter.

It may be seen from experiments that have been made on the genesis of ions by collisions that water vapour does not condense on the negative ions when they are travelling with high velocities under large forces and small pressures. Thus,‡ for values of  $Z/P$  of the order of 50 and upwards, the negative ions in water vapour, at a pressure of 6·5 millimetres, are the same as those in dry gases, and are small compared with positive ions.

\* J. S. Townsend, 'Phil. Trans.,' vol. 193, 1899, p. 148.

† J. Zeleny, 'Phil. Trans.,' vol. 195, 1901, p. 193.

‡ J. S. Townsend, 'Phil. Mag.,' 1903, p. 389 ; 'Phil. Mag.,' 1902, p. 8.

*Measurement of Rotatory Dispersive Power in the Visible and Ultra-violet Regions of the Spectrum.*

By T. MARTIN LOWRY, D.Sc., Lecturer on Physical Chemistry and Instructor in Crystallography at the Central Technical College.

(Communicated by Prof. Armstrong, F.R.S. Received November 3,—Read November 19, 1908.)

The following is a brief preliminary account of improvements effected in the method of determining rotatory dispersive power which have made it possible to observe accurately not only in the bright regions of the visible spectrum, but throughout the scale from the region of the lithium red line into that commanded by the photographic plate.

Two methods have generally been used for the purpose, namely, (1) Broch's method, in which a spectroscope is arranged in series with the polarimeter and a narrow strip of a continuous spectrum is picked out for observation—a method which is much improved by using a constant-deviation spectroscope in place of one of the variable-deviation type,\* and (2) Landolt's method, in which a white light is reduced by means of filters to approximate homogeneity in the red, green, light-blue, or dark-blue parts of the spectrum. Neither method fulfils the fundamental condition that the field of the polarimeter shall be uniformly lighted with monochromatic light—many of the measurements that have been made, therefore, possess only a qualitative value. A much better method is due to the late Sir William Perkin, who introduced the use of a spectroscope-eyepiece as a means of purifying the sodium light, and used it on a limited scale for measuring rotatory dispersive power in the red (lithium), yellow (sodium), and green (thallium) parts of the spectrum.

The method now described resembles Perkin's method in its essential feature, namely, the use of monochromatic or multichromatic light (spectroscopically purified) in place of a band from a continuous spectrum. It has the advantage that it renders available for polarimetric measurements, in addition to the flame spectra, the large series of intense line spectra produced by the metallic arcs, which, with the one exception of the enclosed mercury arc,† do not appear to have been used previously for this purpose. Up to the present, measurements have been made with 26 lines ranging from w.l. 6708 to w.l. 4359; beyond these limits the visual intensity of the light

\* F. Twyman, 'Phil. Mag.,' 1907, vol. 13, p. 481.

† Disch, 'Ann. Phys.,' 1903 (4), vol. 12, p. 1155.

is so small that polarimetric observations become very difficult, but in the intermediate part of the spectrum the list might, without difficulty, be extended considerably. The mercury lines referred to in the table were produced by a Bastian lamp; the copper and zinc spectra were produced by means of copper or brass electrodes rotating in opposite directions, as recommended by Baly in the case of the iron arc; the cadmium spectrum was obtained by means of rotating copper or silver electrodes coated with the metal.

In order to utilise the arc spectra for polarimetric observations, a parallel beam from the arc is thrown on to the widely-opened slit of a constant-deviation spectroscope. An achromatic lens of 22" focus is substituted for the observing telescope of the spectroscope, and is used to cast a magnified image of the slit on to the polarising prisms which produce the horizontally-divided triple field of the polarimeter. By turning the constant-deviation prism to a suitable position, the field can be illuminated from top to bottom by a brilliant band of pure monochromatic light, the maximum width of the band being determined by the openness of the spectrum and, in a very important manner, by the efficiency of the dispersive system. By using a C.D. prism of high density in conjunction with the long-focus lens, it is possible to read separately the two lines 5790 and 5769 which constitute the yellow mercury doublet, although these differ in wave-length by only 21 Ångström units; the yellow doublet and green triplet in the copper spectrum can be read with ease and accuracy as broad bands each occupying a width rather greater than one-third of the 8-mm. aperture of the triple field; the chief lines in the mercury and cadmium spectra can be made to cover practically the whole field without overlapping. In order to eliminate stray light, which would give rise to serious errors in the red and violet readings, a Perkin spectroscopic eye-piece is used.

In measuring rotatory dispersive power in the ultra-violet, a parallel beam of light from an arc formed between a carbon and a magnetite electrode is cast directly by a quartz condenser on to the triple field of the polariser, Foucault prisms being substituted for the Nicol prisms to ensure transmission. A quartz-calcite lens of 13" focus is substituted for the analyser-telescope; this casts a diminished image of the triple field on the slit of an ultra-violet spectroscope. The spectrum thus produced is photographed in the ordinary way by means of a camera provided with a quartz-calcite lens of 22" focus; the division produced by the triple field can be seen clearly, and it is easy to pick out and identify on the negative the line which is of equal intensity in its three sections. By taking photographs with the analyser in different positions

it is possible to determine the rotatory power of a substance throughout the transmitted spectrum.

The results obtained with water, carbon bisulphide, and other liquids in a magnetic field will be dealt with in a later communication; the method is one which is likely to be of special value as affording a means of determining the homogeneity of apparently simple liquids.

The polarimeter readings shown in the table were usually concordant within a few hundredths of a degree: the absolute values may differ by as much as  $1^\circ$  in different specimens of the ester, but the relative values  $\alpha/\alpha_D$  are probably reliable within one or two units in the last figure.

Table of Wave-lengths used in the Measurement of Rotatory Dispersive Power, together with the rotations produced by 100 mm. of Methylic Camphocarboxylate at  $20^\circ$  C.

	w.l.	$\alpha$ .	$\alpha/\alpha_D$ .		w.l.	$\alpha$ .	$\alpha/\alpha_D$ .
Li red .....	6708	48°32	0·728	Cu green .....	5154	94°93	1·430
Cd red.....	6438	53°41	0·805	Cu green .....	5105	97°52	1·469
Zn red.....	6364	54°91	0·827	Cd green .....	5066	98°60	1·486
Na yellow ...	5893	66°37	1·000	Zn blue .....	4811	116°15	1·750
Hg yellow ...	5790	69°40	1·046	Cd blue .....	4800	116°93	1·762
Cu yellow ...	5782	69°83	1·052	Zn blue .....	4722	122°92	1·852
Hg yellow ...	5769	70°09	1·056	Cu blue .....	4705	124°38	1·874
Cu yellow ...	5700	72°38	1·090	Zn blue .....	4680	126°36	1·904
Ag green.....	5469	80°75	1·217	Cd blue .....	4678	126°55	1·907
Hg green.....	5461	80°94	1·220	Cu blue .....	4651	128°34	1·933
Tl green .....	5351	85°59	1·290	Cu blue .....	4587	134°60	2·028
Cu green.....	5219	91°73	1·382	Cu violet.....	4378	157°62	2·375
Ag green.....	5209	92°17	1·389	Hg violet.....	4359	165°07	2·487

*Results of Magnetic Observations at Stations on the Coasts of the British Isles, 1907.*

By Commander L. CHERWYND, R.N., Superintendent of Compasses.

(Communicated by Rear-Admiral A. M. Field, R.N., F.R.S. Received July 14,—  
Read December 10, 1908.)

(Abstract.)

With a view to comparing the values of secular change of declination, horizontal force, and inclination, at various stations on the coasts of the British Isles, with the values derived from the continuous records at Kew Observatory, the Hydrographer (Rear-Admiral A. Mostyn Field, F.R.S.) directed that observations should be made at certain stations selected from those occupied by Rücker and Thorpe during their magnetic survey for the epoch January 1, 1891.

The observers detailed to make the observations were:—Captain M. H. Smyth, R.N., H.M.S. "Research"; Captain W. Pudsey-Dawson, R.N., H.M.S. "Triton"; and Captain J. W. Combe, R.N., H.M. surveying vessel "Gladiator." The stations selected were fairly distributed around the coasts, so that a mean of the results would represent the mean for the whole area embraced.

The observations have been reduced to the epoch January 1, 1907, by means of comparisons with the records at Kew Observatory. The resulting values of mean annual changes for the British Isles are as follows:—

	(a) 21-year period. 1886—1907.	(b) 16-year period. 1891—1907
(1) Declination .....	— 5'·7	— 5'·1
(2) Horizontal force .....	+19 $\gamma$	+18 $\gamma$
(3) Inclination .....	— 1'·6	— 1'·4
(4) Vertical force (excepting the results at Dublin and Tanera Mor) .....	— *	—14 $\gamma$

The mean annual changes of declination at Kew comparable with (1) *a* and *b* are respectively 5'·2 and 4'·9. Thus the mean for the British Isles during the 16-year period is 0'·2 greater than at Kew.

The mean horizontal force change appears to have been 3  $\gamma$  less than at Kew. The mean inclination change during the 21-year period was 0'·1 less, and during the 16-year period 0'·6 less, than at Kew.

The mean vertical force change during the 16-year period has been  $8\gamma$  less than at Kew.

Diagrams showing the mean annual changes at Kew from 1889 to 1904 indicate that the declination change, which since 1894 has been decreasing in amount, is now increasing, and that the probable mean value for January 1, 1907, Kew, is  $4'8$ . For the whole of the British Isles, therefore, the mean value is assumed to be  $5'$ .

The annual increase of horizontal force continues to diminish and is at the present time very small; there has been a very marked diminution during the last two years, and the annual increase may shortly become a decrease.

The annual change of inclination continues to decrease in amount, and is now  $1'$  (nearly).

A comparison of the value of the mean annual change of declination at Kew, Greenwich, and Stonyhurst shows that whereas, during the period embracing Rücker and Thorpe's survey (1886—1894), the change at Stonyhurst was considerably greater than at Kew and Greenwich, this being in accord with the results found by Rücker and Thorpe, that the secular change was greater in the north-west than at Kew.

Since the year 1894, however, the values have been in closer agreement, that at Stonyhurst being slightly less than at Kew. Thus it is indicated that the variations of secular change are not, over the area referred to, synchronous.

Comparisons of results of declination observations made at sea with those made on shore show considerable differences, and although the sea observations cannot be considered to the same degree of accuracy as the shore observations, the differences are in most cases outside the margin which might be assigned to this cause.

The results indicate that the values at sea are, off the east coast generally greater, and on the west coast generally less, than the corresponding values adduced from observations made on shore. It is intended to investigate this subject further.

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*Potential Gradient in Glow Discharges from a Point to a Plane.*

By J. W. BISPHAM, B.A., B.Sc., Research Exhibitioner and former Scholar of Emmanuel College, Cambridge.

(Communicated by Prof. Sir J. J. Thomson, F.R.S. Received November 11,—  
Read December 10, 1908.)

(1) *Description of Apparatus and General Description of Phenomena.*

*Preliminary.*

The original object of the experiment described in this paper was the investigation of the distribution of electric force along the axis of glow discharges from a charged point to a neighbouring plane in the case when striæ are visible. Such discharges are described by V. Obermayer.\* The appearance of the discharge—as Prof. Thomson† has pointed out—suggests that the current is not merely carried by ions of the same sign as the discharging point. Obermayer notes, however, that the type of discharge obtained varies considerably with the capacity shunted across the terminals of the discharge, and also depends on the self-induction in the circuit, indicating that the discharges are of an oscillatory or intermittent character (see fig. 6, A, B, D, and E).

The following experiments lead to the conclusion that *all* the types of striated glow discharge described by Obermayer, in which the glow spreads out from the point to the plate in a more or less conical form, are of an intermittent character.

Speaking generally, it was found that in the case of hydrogen, when the pressure was about 1 cm. of mercury, two types of continuous discharge were possible, one for small currents and the other for larger currents. In the first there was only luminosity in the neighbourhood of the point. But for larger currents, both for positive and for negative direction of the current, this point glow form changed over unstably to another form, in which a much lower E.M.F. maintained the larger current, and the form of discharge was then that obtained between small plane electrodes. See fig. 6 (E and F). With a large external resistance in circuit an intermediate unstable condition could be examined in which the discharge was intermittent (fig. 6, A, B, D, and E).

*Apparatus.*

The distribution of electric force along the axis was obtained by first observing the distribution of potential along the axis, and hence deducing the

\* V. Obermayer, 'Wien. Sitzungsberichte,' c.p. 127, 1891.

† J. J. Thomson, 'Conduction of Electricity through Gases,' 1st ed., p. 411.



electric force graphically. For this purpose it was necessary to produce relative axial motion of the exploring electrode and discharge.

In the apparatus finally used, the explorer remained stationary and the discharge was moved past it on geometrical guides.

The discharge apparatus was enclosed in a large bell-jar 12 inches high and of 8 inches diameter (fig. 1). The whole discharge apparatus was supported

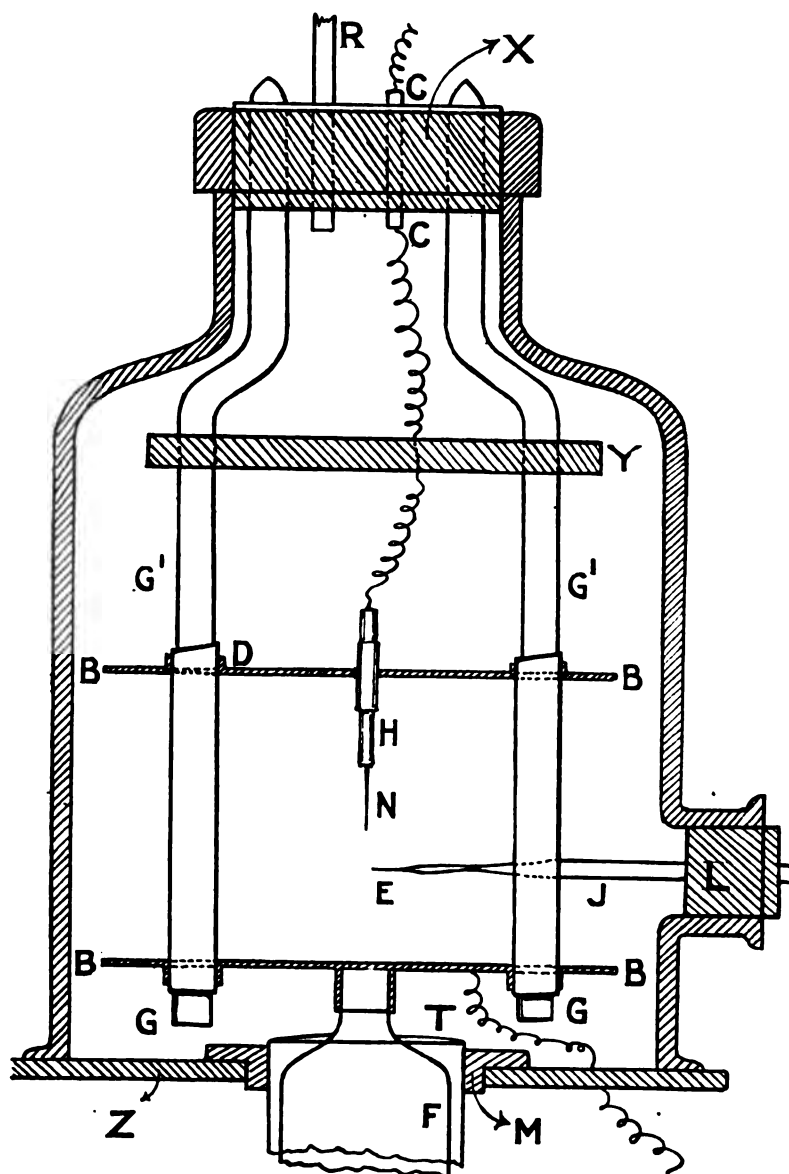


FIG. 1.

on a large glass cylinder which floated on mercury. The motion of a mercury surface exposed to the atmosphere produced similar motions of the mercury surface at almost barometric height above it. The latter surface floated the discharge, and was itself in contact with the rarefied gas under observation.

Two brass plates, 12 cm. in diameter and 1 mm. thick, were fixed at a distance of 7.5 cm. apart by three glass tubes, cemented into three collars on the outer side of each plate.

Another brass collar, of internal diameter 4 mm., pierced the upper plate at its centre and passed through at right angles to its surface, extending about 1 cm. on either side.

In this collar slid a brass rod to the end of which the discharge needle was soldered axially. This arrangement furnished an adjustable electrical contact between the point and the upper plate. The discharge point and the lower plate were fixed relatively during the experiments, but the *whole system* was moved up and down by flotation on mercury. Attached to the lower plate by a central brass collar was a long cylindrical glass bulb which floated on mercury in a coaxial glass cylinder with a clearance of 2 mm. A rubber U-tube connected the outer cylinder with a reservoir of the type usually employed for Toepler pumps. Its vertical motion was controlled by suspending it from a string fixed to the circumference of a pulley. The pulley was screwed tightly back against a wooden surface, so that it was held by friction in any position in which it was left. The pulley was adjusted by hand, and it was found possible to produce very small motions of the discharge.

The three glass tubes previously mentioned as holding the parallel plates apart also served as movable guides for the motion. Through these tubes ran three other tubes of stout glass of smaller diameter. The inner tubes ( $G'$ ,  $G$ , fig. 1) forming the fixed guides passed eccentrically through the movable ones, and a vertical line of contact was formed between each pair which served as a geometrical guide. This arrangement also possessed the advantage that the guides were on the same level as the actual displacement required, and so completely controlled it. When viewed through a cathetometer it was seen that the relative motion of the exploring electrode and discharge point was very accurately parallel to the vertical cross wire. The motion was very slow and steady by reason of the damping due to the viscous and surface resistances of the thin annulus of mercury between the float and its concentric chamber.

The cylindrical float was loaded with lead shot at its lower end to make its displacement more definite, to steady the motion, and to locate the

inertia of the movable system more nearly at the point of application of the hydrostatic forces.

The three tubes which formed the fixed guides  $G$ ,  $G_1$  were securely cemented by a mixture of resin and beeswax into three vertical holes in an ebonite stopper ( $X$ ), closing the neck of the bell-jar.

The guides were also fixed relatively at a lower point by another piece of ebonite ( $Y$ ). The fixed guides were thus knit rigidly together. The bottom of the bell-jar was closed by a stout zinc plate ( $Z$ ) cemented to the flat glass welt of the jar.

In the centre of the zinc plate was a circular hole with an ebonite collar ( $M$ ) to receive the chamber which contained the float.

A glass tube ( $R$ ) cemented through the ebonite stopper in the neck of the jar served as an inlet for gases, while a brass rod ( $C$ ) also cemented through the stopper allowed electrical contact to be made with the discharge needle through a spiral of wire soldered to it and to the rod carrying the discharge needle.

The brass plate forming the flat electrode was connected by a loose spiral of copper wire with the stout zinc plate, closing the bottom of the jar.

In the experiments the flat electrode was always earthed and the needle charged to a high potential by a Wimshurst machine, or by a large battery of lead cells.

#### *The Exploring Electrode.*

Earlier experiments were made with another form of apparatus in which the exploring electrode was a ring of wire arranged to move with its centre on the axis of discharge. This form was subsequently discarded, because it was necessarily of a size large enough to produce quite marked disturbances in the electric field between the point and plate. The form finally adopted was similar to that used by H. A. Wilson\* in his experiments on potential gradient between plane electrodes.

A fine platinum wire  $E$ ,  $1/1000$  inch in diameter, was covered by a very fine capillary tube of glass to within  $1/5$  mm. of its tip.

The apparatus was exhausted by means of a Toepler mercury pump, and the pressures were read by a McLeod gauge which normally gave a magnification of 38. These are not indicated in diagrams, as they presented no peculiar features. The apparatus was kept dry by two phosphorous pentoxide bulbs, and the hydrogen and air used were respectively passed through sulphuric acid and dry granulated calcium chloride to dry them before they entered the apparatus at all. The hydrogen was prepared from

\* H. A. Wilson, 'Phil Mag.', vol. 49, p. 505, 1900.

pure sulphuric acid and pure zinc. In the earlier experiments the hydrogen was washed through permanganate solution. But the gas always behaved after sparking as if it were moist, and it was suspected that oxygen was carried over with the hydrogen.

In subsequent experiments the pressure remained constant for days and consistent readings were obtained.

*Electrical Connections.*

The circuit was a very simple one and is shown diagrammatically in fig. 2.

A battery B had one terminal earthed through a lead  $L_1$ .

Its high potential terminal was connected to the discharge point P through an adjustable resistance R. The plate electrode was connected to earth directly or through the telephone T and galvanometer G.

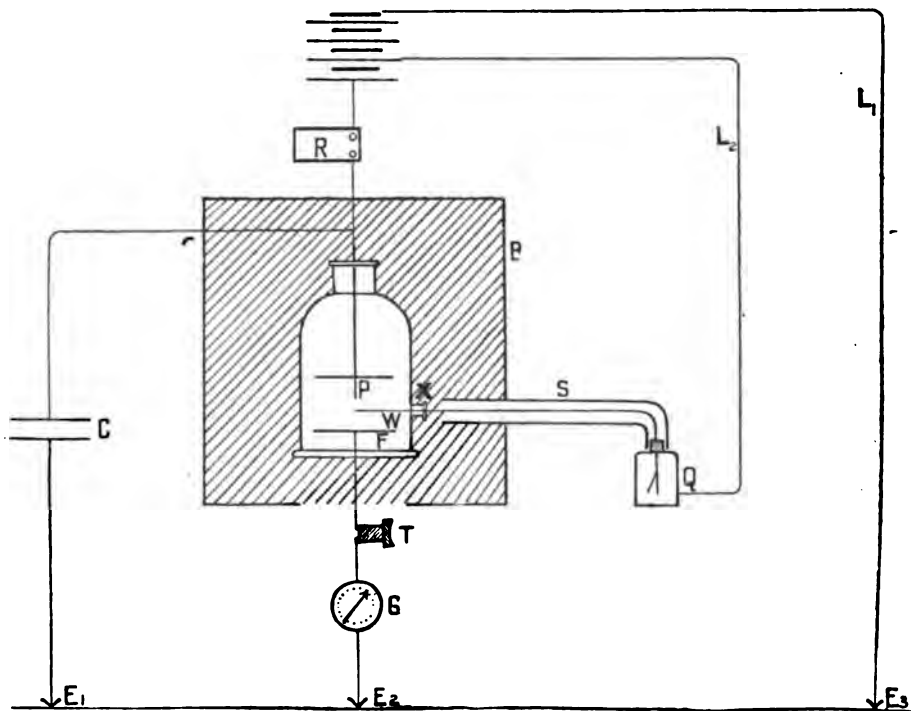


FIG. 2.

If necessary, a condenser C, with one terminal earthed ( $E_1$ ), was connected to P, so as to shunt the main circuit as shown. The exploring electrode X was connected by a wire W in a shielding tube S to the leaf of the gold-leaf electroscope Q.

The case of Q and the shielding tube S were connected by a lead  $L_2$  to an intermediate point on the battery B. The movements of the gold leaf were observed by means of a microscope with 100 divisions in the eye-piece scale. The external high resistance consisted of two parts—a megohm coil adjustable by tenths of a megohm and an electrolytic resistance continuously adjustable from zero to several megohms. The electrolytic resistance was mainly used for producing rapid changes of resistance in making observations of effects. In taking potential curves, the coil was used whenever possible, as the liquid resistance increased with time to a maximum. The current obtained from a battery of small storage cells was remarkably constant, and under these conditions it was particularly easy to obtain steady and reliable readings of the potential from point to point in the discharge.

#### *Measurement of Potential.*

The pressures used in these experiments were fairly high, generally of the order of 1 cm. of mercury, and hence the potential fall between point and plate was of the order of 1000 volts, and never less than 300 volts, of course.

It was accordingly necessary to devise a method for measuring the potential accurately to a volt over a range of 1000 volts.

The method employed was as follows:—The exploring point was connected by means of shielded wires to the leaf of a gold-leaf electroscope. A potential difference of 120 volts deflected the gold leaf to such an angle that it was just off the eye-piece scale of the microscope used to view it. There were a hundred divisions to the eye-piece scale, and a gold leaf was cut which was found on calibration to move roughly 1 division per volt, when the potential difference between the case and the leaf was between the values of 40 and 100 volts. The potential of the electroscope case *could be brought to any required value by connecting it by another lead  $L_2$  to an intermediate point on the battery supplying the discharge current* (see fig. 2). The battery maintained its potential when supplying the small currents used in the experiments, and it was found by testing from time to time that the cells remained very steady for a week at a time, each 20 cells giving consistently 41 volts as measured by a Weston voltmeter. The shielding tubes around the wire leading from the exploring point to the gold-leaf electroscope were electrically connected by soldered wires with the electroscope case, and the case and tubes carefully insulated.

In taking a reading, the shielding tubes and electroscope case were raised to such a potential that the gold-leaf image was always on a calibrated

portion of the scale of the microscope eye-piece. In making a detailed exploration of a small portion of the field, as, for instance, the region from a striation to its neighbour, all the readings were on the scale, and the potential of the case needed no adjustment. This allowed an accuracy of 0.1 of a volt (eye estimated) over a range of 60 volts at least. The capacity of the electroscope system was very small indeed, only a few centimetres.

On moving the discharge relatively to the exploring electrode, the gold leaf moved rapidly up to within a division or so of its final position, and then crept slowly to its final equilibrium position. This occurred when the motion was either upward or downward and the positions finally assumed were identical for currents larger than  $10^{-6}$  ampere.

The exploring electrode used produced no visible disturbance of the discharge and the results justified the conclusion that the disturbing effects were small, except in cases in which the discharge was intermittent.

*Glow limited to Neighbourhood of Point (Hydrogen).*

For small currents and fairly large pressures the glow was confined to the immediate neighbourhood of the point.

The results of the experiments are expressed as curves in which the ordinates are electric force and the abscissa distance from the point.

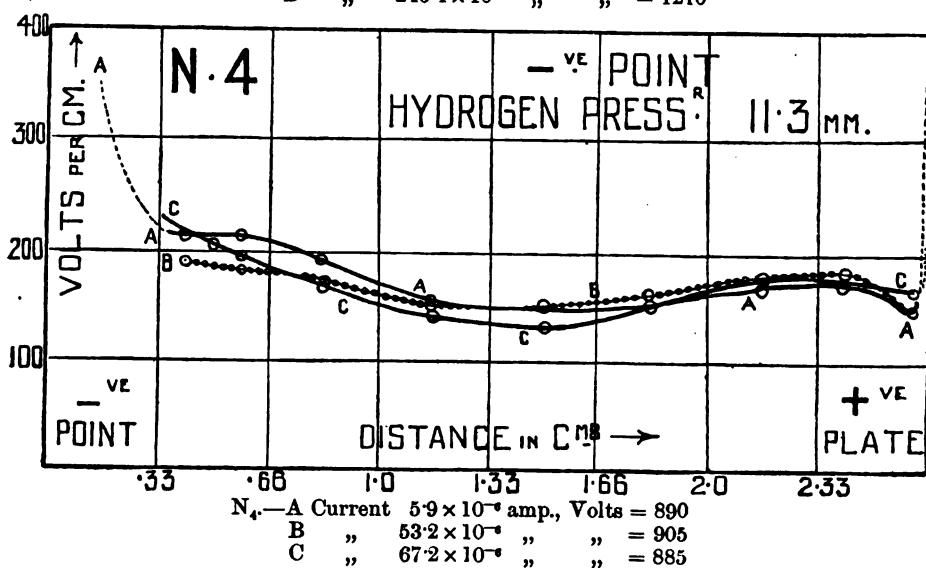
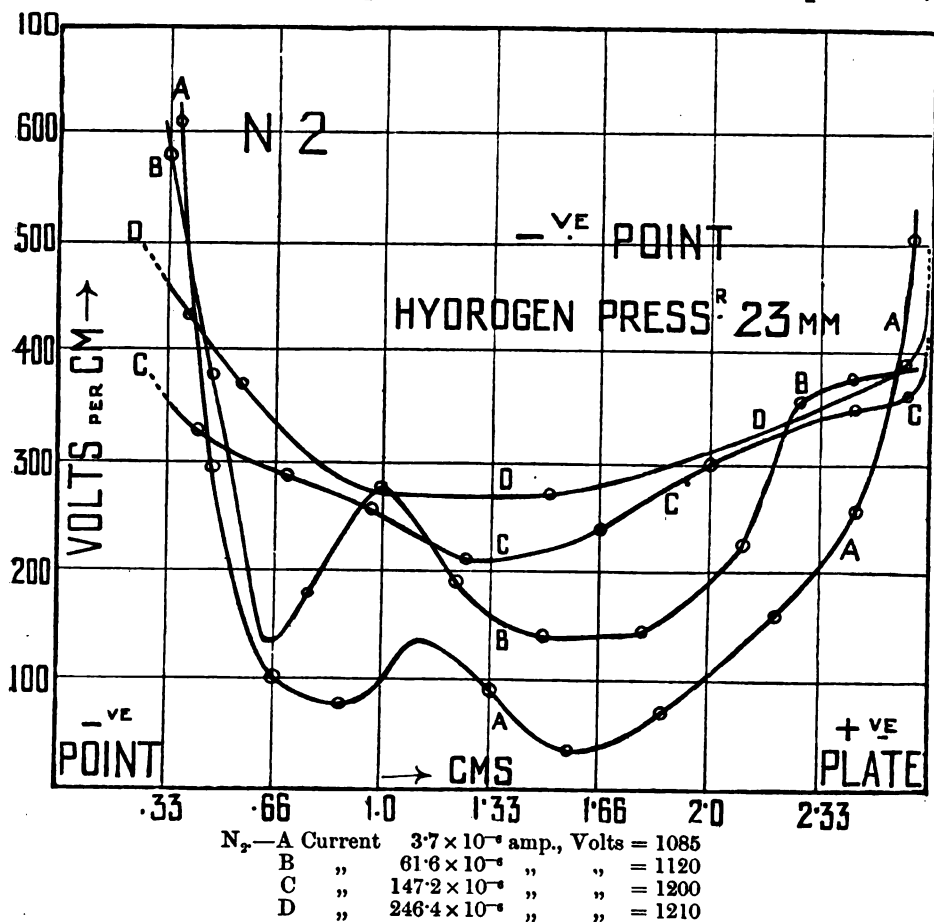
The diagrams for positive point discharges are named  $P_1$ ,  $P_2$ , etc., and those for negative point  $N_1$ ,  $N_2$ ,  $N_3$ , etc., and they will be referred to by these names. Only a few of those taken have been included.

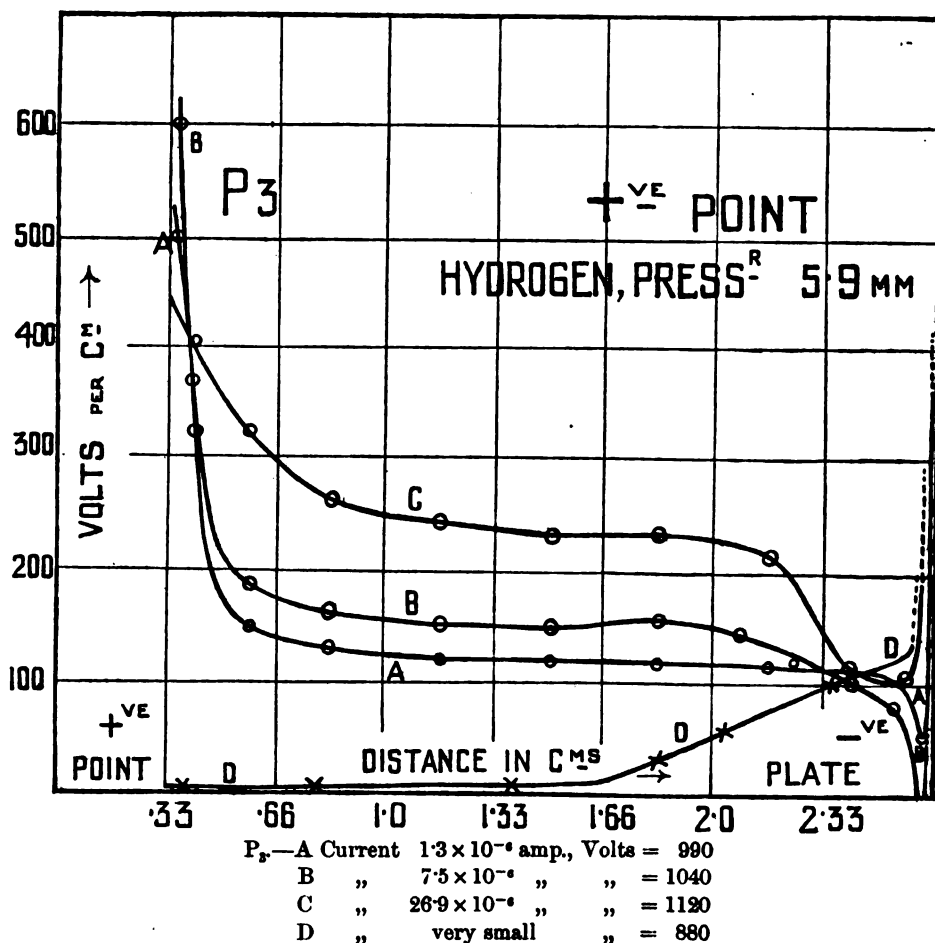
A particular diagram, e.g.,  $P_3$ , refers to results obtained at a particular pressure and the different curves refer to discharges with different values of the current.

All the curves refer to a stable condition, that is, the E.M.F. increases as the current increases. It is seen at once that midway between point and plate, the *electric force increases as the current increases*. This is shown typically in diagram  $P_3$  which gives the curves obtained from a set of readings in hydrogen at a pressure of 5.9 mm. The curves A, B, and C refer to discharges in which the currents flowing were:—

A .....	$1.3 \times 10^{-6}$ amp.,	P.D.	990 volts.
B .....	$7.5 \times 10^{-6}$	„ „	1040 „
C .....	$26.9 \times 10^{-6}$	„ „	1120 „

D refers to a slightly different pressure, the discharge was non-luminous and the current too small to measure. For small currents the fall of potential is almost entirely limited to the regions very near the electrodes.





Experiment showed that this form of discharge—point glow—was only stable within a narrow range of pressures, and even then only for a limited range of current variation.

A greater variation in the value of the current was possible in the case of the higher pressures—indeed, at a low enough pressure (about 3 mm. for positive point and 11.3 mm. for negative point) this form of discharge was unstable. The current passed in an intermittent manner as indicated by a telephone in circuit.

Corresponding to this fact, by examination of the curves (see figs.  $N_3$ ,  $N_4$ ,  $P_3$ , etc.) it is seen that for pressures well in excess of those mentioned, there is a marked difference between the electric force curves for large and small currents, whereas for pressures approximating to those mentioned the curves for large and small values of the current are almost coincident (see fig.  $N_4$ ).



In fig. N<sub>4</sub> the condition of instability has already appeared, for on referring to the figures it is seen that the largest current requires the least terminal voltage to maintain it.

The transmission of current always became intermittent if the current was sufficiently increased. Further increase of electrical transfer was accompanied by a fall and not a rise of terminal potential difference. The glow gradually took up the conical form shown in fig. 6, A and D, and the telephone emitted a loud note. Further increase of current finally produced a discharge which was continuous and stable, the glow being very bright (fig. 6, C and E).

In the case of negative point discharge, for example, for small currents, a glow on the point was obtained.

As the current was increased the telephone began to sing for a definite value of the current, and then the discharge spread away from the electrodes until a general faint luminosity was apparent between the point and the plate. This ultimately took the form of a positive column extending from the plate—a dark space and a negative glow encircling the discharge needle. Further increase of the current caused the positive column to recede to a flat disc of luminosity on the plate. Still further increase of current caused the luminosity on the needle to extend all over the cathode. The experiments point to the condition “point glow” being a form of discharge only possible for certain limits of pressure and current. Within the limits of pressure for which it is stable, *increase of current*, produces ultimately an *intermittent form of discharge*. *Decrease of pressure* ultimately leads to this *intermittent discharge* again, even for the smallest currents. It was not possible with the available voltage to test higher pressures.

Some experiments were made in cases in which the discharge was non-luminous by reason of the extreme smallness of the current. In these cases the potential curves were of the form shown in D, diagram P<sub>3</sub>, which give an actual case observed.

The fall of potential was limited to the immediate neighbourhood of the electrodes. Curves such as A and B, fig. N<sub>2</sub>, would tend to indicate that the discharge in some cases consists of two parts, a discharge from the point to the surrounding gas and another from the gas to the plate. Small variations in the potential curves are associated with relatively large variations in the electric force curves, so that the point must not be unduly emphasised; but the form of curve is a very general one for these sets of readings, and the point is therefore worth consideration. Many curves of the same type were obtained.

*The Intermittent Positive Discharge without Striae (Fig. 6, A).*

As has been pointed out, with a high resistance in circuit it was possible to obtain an intermittent discharge for currents intermediate in value between those accompanying "point glow" and the steady discharge form represented in fig. 6, C.

This intermittent form is represented typically in fig. 6, A. It was noted that the negative glow was a doublet divided into two portions by a dark interval  $p$  (fig. 6, A), although the Faraday and Crookes dark spaces were quite typical. As the pressure was reduced, the whole doublet moved away from the cathode. Potential readings were taken at various pressures and curves plotted. The curves were all of one type, there was an apparent reversal of field between the surface of the negative glow next the cathode and the dark interval ( $p$ ) referred to above. That is to say, the surface of the negative glow corresponded to maximum and the layer ( $p$ ) to a minimum of potential. The curves obtained are not published, as they are of exactly the same type in this particular as the portion AA' of the curve of fig. 3.

With all external inductances and capacities removed, the discharge retained the same character, and for large currents a note could be heard without the telephone in circuit. The readings of potential—the apparent reversal referred to above—probably depended on the capacity of the electroscope system. Probably the potential as each intermittent discharge occurred tended to rise to a certain value, and the actual reading depended on the number of ions present to convey electricity to and from the exploring point.

A test established this to be the case. It was found that whereas the readings of the electroscope were independent of its capacity for continuous discharges, whether the current was large or small, for intermittent discharges the potential curves *did* depend on the capacity of the electroscope system. Readings are given which were made to test this point. Increase of capacity was found to increase the maximum of potential, such as A, fig. 3, and decrease the minimum of potential (A', fig. 3). *Increase of the capacity of the electroscope system thus increased the distortion of the curve.*

*Readings.*

Four readings were always made alternately with and without augmented capacity of the electroscope, of the maximum and of the minimum potential:—

	Volts.	
	Maximum.	Minimum.
With condenser on electroscope .....	292.5 (mean)	239.5 (mean)
Without condenser .....	282.5 „	248 „

The results might be explained by supposing an excess of negative ions at the minimum of the curve, and an excess of positive ions at the points corresponding to the maxima. The maxima were found to correspond very closely to the surface of the negative glow nearest the cathode, while the minima were closely in agreement with the dark interval (*p*) which divided the negative glow into a doublet. A similar apparent reversal of field was obtained near the point in the case in which the point was made the cathode. The apparent reversal seems clearly to be due to the *positive electrification of the Crookes dark space*, and to an excess of negative electrification at a point farther away from the cathode. At some intermediate point in the negative glow the number of ions of opposite sign are equal. A similar series of apparent reversals were obtained in plotting the potential curves from stria to stria in the striated form of discharge. (See fig. 3.)

#### *Intermittent Discharge with Striæ—Hydrogen.*

When a condenser was shunted across the terminals of the discharge, and the total E.M.F. applied through an external resistance was greater than that necessary to maintain the discharge, the discharge passed in an intermittent manner. The period became very large when the condenser used had a capacity of a microfarad. By adjusting the resistance the period became as long as 1 second, and the discharge passed by a brilliant flash of such intensity as to cause anxiety for the safety of the apparatus. This flash was followed by an interval of darkness for a second, and then another such discharge occurred. By decreasing the shunted capacity and decreasing the series resistance, the period could be steadily reduced until the note was of a pitch so high that it passed out of the range of audibility, as indicated by the telephone in circuit. Under these conditions, striæ (fig. 6, B) were generally observed. It was noted that the distance apart of the striæ did not perceptibly change (in this particular type of discharge) when quite large changes in current were made, whereas, in the steady and continuous forms of discharge (fig. 6, C) the disposition of the striæ changed very rapidly as the current was varied. An attempt was made to obtain potential curves under these conditions.

Both curves (figs. 3 and 4) refer to hydrogen. The discharge from the negative point was first examined, and the potential curve obtained was of the form shown, fig. 4. On this diagram, both the potential and the corresponding electric force curves are given. The electric force curve is probably unreliable, to judge from the type of potential curve obtained in the case of the positive discharge (fig. 3). But it was observed that the fall of potential was steep in the bright parts of the striæ, and flat in the intermediate dark layers. It is probably more easy to interpret the results

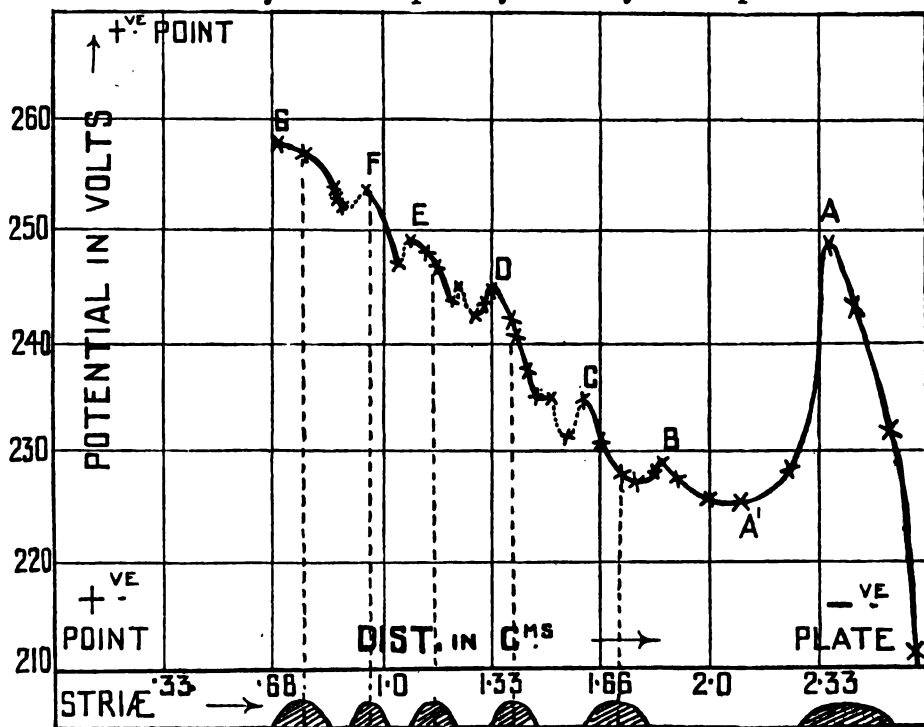


FIG. 3.

by reference to the diagram, fig. 3, in which the results for positive discharge are given. The maximum A of the curve is of the type previously described (in the case of the curves of intermittent discharges without striæ) and has been shown to depend on the capacity of the electroscope measuring the potential. Both the maximum A, and the minimum A', are exaggerated by increasing the capacity of the electroscope, A then probably corresponds to a region of positive electrification and excess of positive ions, while A' corresponds to a region of negative electrification. Probably each of the maxima B, C, D, etc., are of the same type and correspond to regions of resultant positive electrification while the corresponding minima refer to regions of negative electrification.

Referring still to the case of positive discharge, fig. 3, it is seen that on this supposition there is an excess of positive electrification on the anode side of the bright portion of a stria, and an excess of negative electrification on the cathode side of the bright part of the stria. In fig. 3, the apparent reversal is dotted if no intermediate point on the curve was obtained. In the case of the negative glow, it is seen that there is an excess of positive electrification on the Crookes dark space side of the negative glow, while in the Faraday dark space negative electrification is in excess. If the same line of reasoning

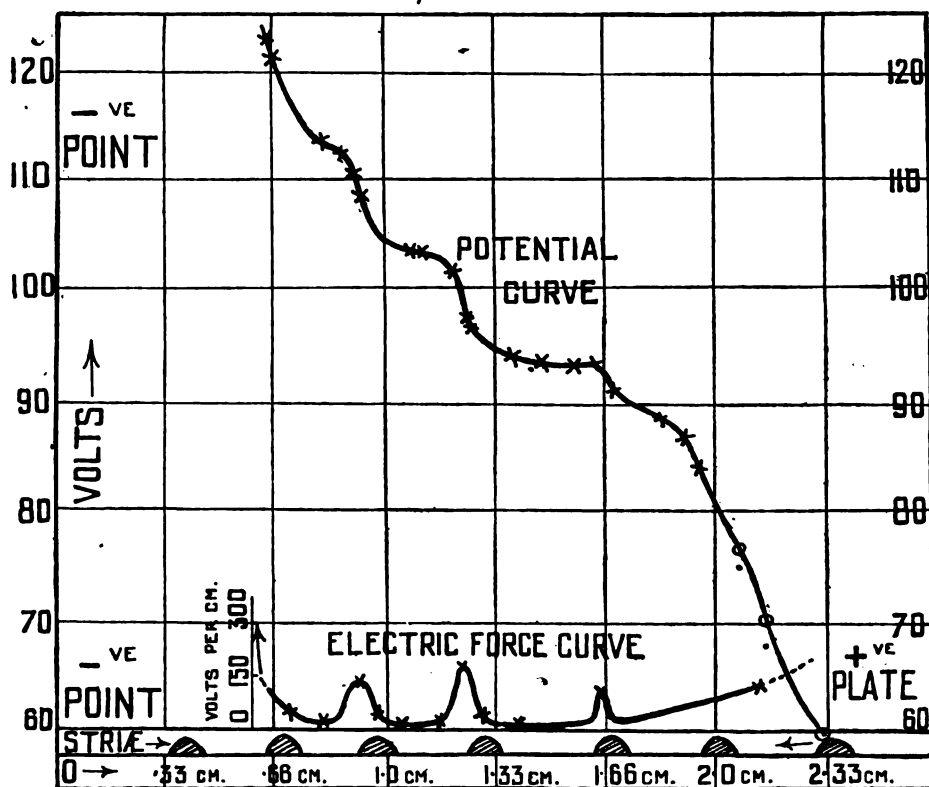


FIG. 4.

be applied in the case of the discharge from the negative point, it is seen that the curve should have a more uniform slope if these positive and negative excesses of electrification did not affect the electroscope. The excesses of positive and negative electrification are very much more marked in the case of the discharge from positive point than in the case of the discharge from negative point. It is possible that equalisation of potential is much more rapid when the discharge is occurring from a negatively charged point, because the negative ions are then in excess on the whole and they have a

smaller mass and are more mobile than the positive ions, so that the local discrepancies are less marked.

The curves seem to be more reliable as indicating *resultant electrification* than as potential curves pure and simple. The curve for negative point perhaps approximates to the truth. It refers to a discharge in which the pressure was 3.9 mm. and the current  $1.2 \times 10^{-4}$  ampere. Fig. 3 for the striated discharge from positive point refers to the same pressure 3.9 mm., the current being  $1.6 \times 10^{-4}$  ampere and the average potential difference across the terminals being 800 volts.

*Continuous Discharge for Large Currents—Air (Fig. 6, C and F).*

As has been previously pointed out, the smallest currents at certain pressures were accompanied by a discharge in which luminosity was only appreciable near the point. Increase of current produced an intermittent discharge in which the terminal potential decreased as the average current increased. Still further increase of the current produced a discharge in which a large current was maintained by a terminal potential difference much less than was necessary to maintain the small current of the "point glow" type of discharge. It is obvious that in the absence of the large external resistance which was always in series during the experiments, that the first condition would have passed over spontaneously to the second. The resistance in question rendered possible an intermittent and otherwise unstable condition of flow. The distribution of potential was examined for these *larger* currents, and the curves obtained point to the view that the point and a small area of the plate acted merely as small electrodes and that there was very little real modification of the discharge due to the point. The platinum needle apparently acted as a cylindrical electrode merely. The appearance of the discharge also tended to support this view. When the platinum needle was made the cathode, the negative glow which surrounded it was of the lipped test-tube shape examined by Prof. H. A. Wilson.

The positive column extended from the plate towards the point and was separated from the negative glow by a typical Faraday dark space. The luminosity, however, was limited to a narrow axial pencil and apparently the current did not flow from any but a limited area of the anode plate. On increasing the current, the negative glow grew so as to envelop more of the cathode, while the positive column slowly shortened and retreated till it was merely represented by a very bright circular disc of light on the centre of the plate. When the point was negative, striæ were never obtained with these larger currents, but when the point was positive, striæ were obtained, the discharge still being limited to a narrow pencil (fig. 6, C).

With the point positive the discharge again presented the typical appearance, an almost cylindrical positive column extending from the point towards the plate. A brilliant and somewhat peculiar negative glow at an unusually large distance from the cathode was separated from the above mentioned positive column by the usual Faraday dark space. On increasing the current the positive column became striated, and on still further increasing the current the positive column shrunk back, stria by stria, into the point anode, until only a brilliant light on point and plate remained. Meanwhile, the negative glow had spread itself over the whole plate. Unfortunately, in the case of hydrogen, the narrow pencil of discharge was often not axial. Apparently the dimensions of the apparatus introduced an instability for this type of discharge when it occurred in hydrogen. No such instability was observed in the case of air.

Sets of readings were taken for the distribution of potential (both for positively and negatively electrified point) in discharges for relatively large currents in air.

The curves are not given, as they exactly resembled those obtained by Prof. Wilson for ordinary discharges. The curves served to indicate, however, that the exploring electrode was acting in a constant and reliable manner. When the plate was cathode the curves very clearly indicated that the *cathode fall was continuous throughout the dark space*. On making the plate positive the anode fall of about 35 volts was very abrupt.

A constant cathode fall of 340 volts was obtained—the cathode being lead. The cathode fall was independent of current and pressure for large changes and was scarcely increased when the point was made cathode, indicating that the influence of the “point” was no longer very great.

The electric force in the negative glow was very small indeed. The curves gave very satisfactory testimony as to the efficiency of the explorer.

#### *Abnormal Thickness of the Dark Space in Air and Hydrogen.*

For these readings the plate was always made the cathode. The boundary of the negative glow (both for large continuous currents and also for the oscillatory types of discharge described above) was definite and constant, and as it was very nearly parallel to the cathode plate, readings of considerable accuracy were possible, until the pressure became so low that the boundary was no longer distinct.

The thickness of the dark space was measured by the movement of the discharge necessary to bring first the plate and then the boundary of the negative glow into coincidence with the exploring point. The appearance of the negative glow was extraordinary for large steady currents, and

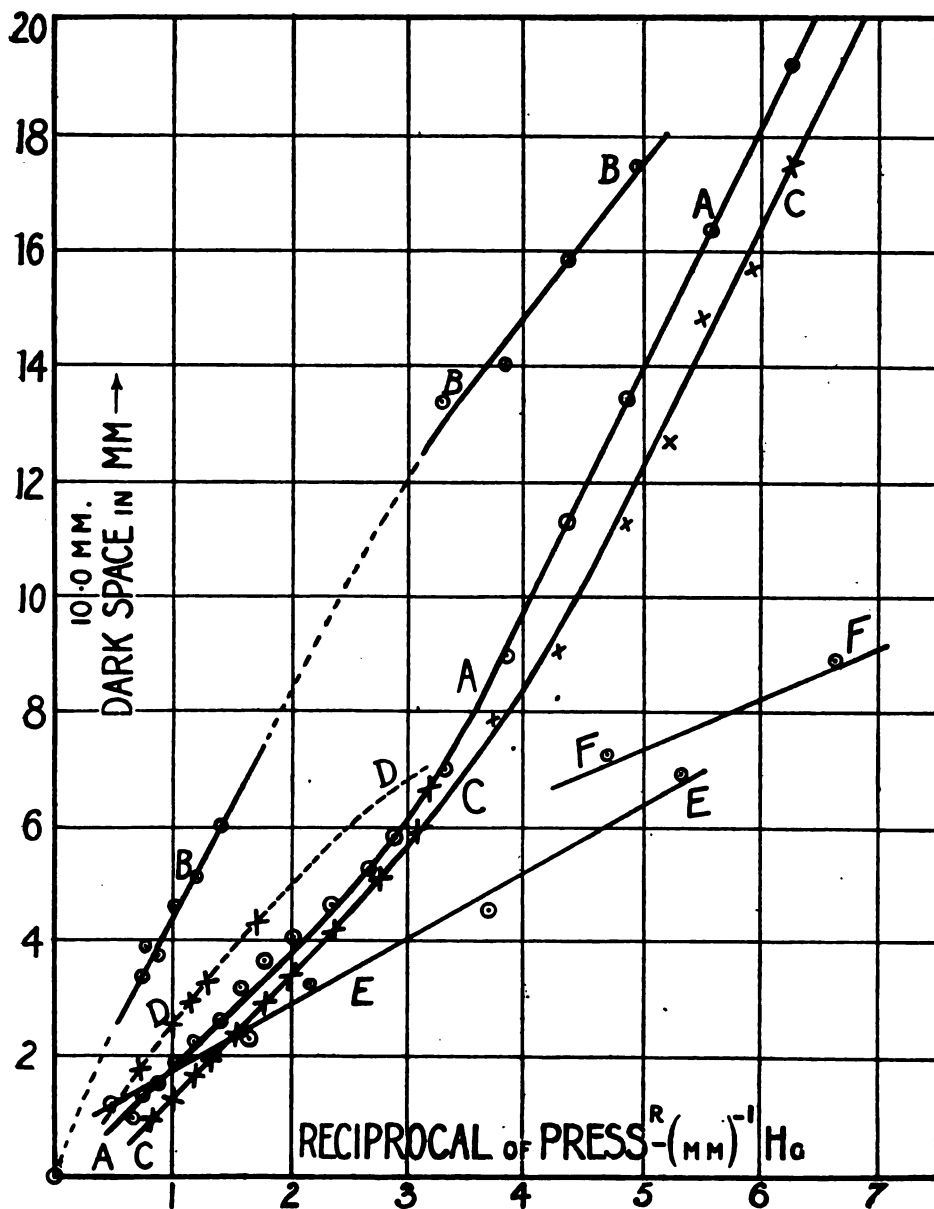


FIG. 5.—Cathode space in air.

deserves special mention. The negative glow was of the form represented diagrammatically in fig. 6, C. It closely resembled one of the striæ of the positive column ( $m$ ) embedded in a blue halo ( $n$ ) in the case of hydrogen. The striæ and the central portion of the negative glow were of a bright salmon-red colour. The negative glow was surrounded by a blue halo.



Moreover, the cathode dark space was unusually large, and instead of being *concave*, the negative glow, like the striæ, was *convex* to the cathode, as was also noticed in the case of the intermittent type of discharge. Some results will be detailed for the case of air. The thickness of the dark space was measured to the strongest line of demarcation between the glow and the dark space. In the case of the continuous discharge as shown in fig. 6, C, the reading to the boundary of the blue halo ( $n$ ) gave a very different value from the reading to the strong line of demarcation which divided the red glow  $m$  from the blue halo. Sets of readings were taken and curves drawn to compare the values of the dark space with those obtained by Ebert\* and Ashton†.

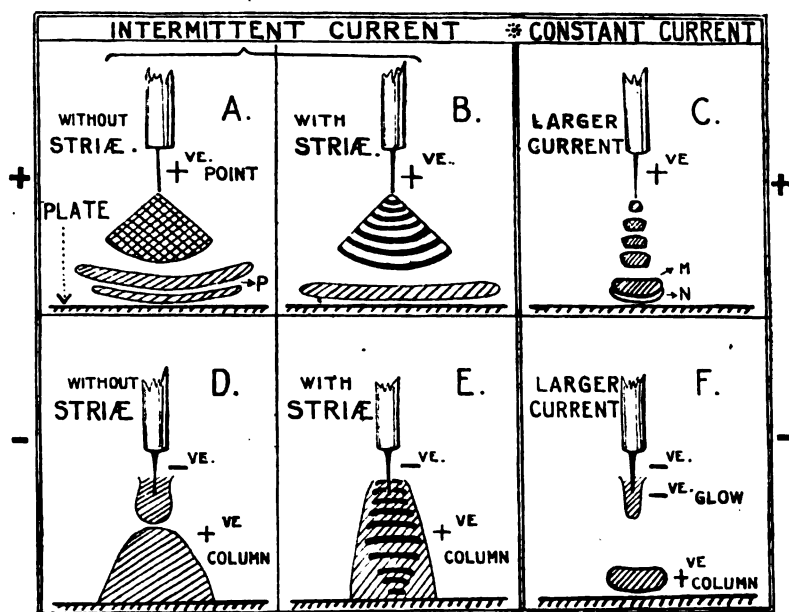


FIG. 6.

The curves were of similar type, but the values obtained, both in air and hydrogen, were uniformly greater than those of Ebert and Ashton. Thus in fig. 5 the curves BB and DD refer to measurements in air for large steady currents (BB up to red glow, DD to the vague blue halo). Curves CC and AA refer to intermittent discharges respectively with and without condenser shunted in. EE and FF are the values obtained by Ebert and Ashton. As has been mentioned, the negative glow was unusual in appearance, and

\* Ebert, 'Wied. Ann.,' vol. 19, pp. 200, 372, 1899; and 'Verhand. Deutsch. Physik. Ges.,' vol. 2, p. 99, 1900.

† Ashton, 'Roy. Soc. Proc.,' April, 1907.

looked—in the case of large steady currents—like a stria embedded in a blue-halo.

The unusually large values of the cathode dark space indicated by the curves may be due to the proximity of the point, or to the large size of the cathode as compared with the distance between the electrodes, but these points have not been investigated. The readings were taken because it was observed that the cathode space was unusually large. It was impossible to continue the investigation. Some diagrams of discharges are given in fig. 6.

The above experiments were carried out at the Cavendish Laboratory, Cambridge, and I am much indebted to the inspiration of that Institution, and more particularly to Prof. Sir John Thomson for his constant interest and advice.

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## MINUTES OF MEETINGS.—SESSION 1908-9.

*November 5, 1908.*

Sir WILLIAM CROOKES, Vice-President, in the Chair.

The Right Hon. Herbert Henry Asquith and His Grace the Duke of Bedford were balloted for and elected Fellows of the Society.

The following Papers were read :—

- I. "Note on Tidal Bores." By LORD RAYLEIGH, O.M., Pres. R.S.
- II. "Vortices in Oscillating Liquid." By LORD RAYLEIGH, O.M., Pres. R.S.\*
- III. "Note on Two Recently-compiled Calendars of Papers of the Period 1606—1806 in the Archives of the Royal Society." By Prof. A. H. CHURCH, F.R.S.
- IV. "On the Generation of a Luminous Glow in an Exhausted Receiver moving near an Electrostatic Field, and the Action of a Magnetic Field on the Glow so produced; the Residual Gases being Oxygen, Hydrogen, Neon, and Air. Part 3." By the Rev. F. J. JERVIS-SMITH, F.R.S.
- V. "The Rate of Production of Helium from Radium." By Sir JAMES DEWAR, F.R.S.\*
- VI. "The Spectrum of Radium Emanation." By A. T. CAMERON and Sir WILLIAM RAMSAY, K.C.B., F.R.S.\*
- VII. "On the Osmotic Pressures of Aqueous Solutions of Calcium Ferrocyanide. Part I.—Concentrated Solutions." By the EARL OF BERKELEY, F.R.S., E. G. J. HARTLEY, and C. V. BURTON.
- VIII. "The Effect of Pressure upon Arc Spectra. No. 2.—Copper." By W. G. DUFFIELD. Communicated by Prof. E. RUTHERFORD, F.R.S.
- IX. "On a Method of comparing Mutual Inductance and Resistance by the Help of Two-phase Alternating Currents." By A. CAMPBELL. Communicated by Dr. R. T. GLAZEBROOK, F.R.S.

\* Received and published during Autumn Recess.

*November 12, 1908.*

Sir WILLIAM CROOKES, Vice-President, in the Chair.

The following Papers were read :—

- I. "The Charges on Ions in Gases, and the Effect of Water Vapour on the Motion of Negative Ions." By Prof. J. S. TOWNSEND, F.R.S.
- II. "The Charges on Ions produced by Radium." By C. E. HASELFOOT. Communicated by Prof. J. S. TOWNSEND, F.R.S.
- III. "The Occlusion of the Residual Gas and the Fluorescence of the Glass Walls of Crookes Tubes." By A. A. CAMPBELL SWINTON. Communicated by Sir WILLIAM CROOKES, F.R.S.
- IV. "An Investigation on the Anatomical Structure and Relationships of the Labyrinth in the Reptile, the Bird, and the Mammal." By Dr. A. A. GRAY. Communicated by Prof. J. G. MCKENDRICK, F.R.S.
- V. "The Natural Mechanism for evoking the Chemical Secretion of the Stomach. (Preliminary Communication.)" By Dr. J. S. EDKINS and Miss M. TWEEDY. Communicated by Prof. E. H. STARLING, F.R.S.
- VI. "Further Observations on Welwitschia." By Prof. H. H. W. PEARSON. Communicated by Prof. A. C. SEWARD, F.R.S.
- VII. "On the Presence of Hæm-agglutinins, Hæm-opsonins, and Hæmolysins in the Blood obtained from Infectious and Non-infectious Diseases in Man. (Preliminary Report.)" By L. S. DUDGEON. Communicated by Prof. T. G. BRODIE, F.R.S.
- VIII. "Preliminary Note on the Occurrence of a New Variety of Trypanosomiasis on the Island of Zanzibar." By A. EDINGTON. Communicated by Prof. J. ROSE BRADFORD, For. Sec. R.S.

November 19, 1908.

Sir WILLIAM CROOKES, Vice-President, in the Chair.

Prof. C. H. Lees, Prof. A. Liversidge, and Dr. Teall were elected Auditors of the Treasurer's Accounts on the part of the Society.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair.

The following papers were read:—

- I. "Memoir on the Theory of the Partitions of Numbers. Part IV.—On the Probability that the Successful Candidate at an Election by Ballot may never at any time have Fewer Votes than the One who is Unsuccessful; on a Generalisation of this Question; and on its Connection with other Questions of Partition, Permutation, and Combination." By Major P. A. MACMAHON, F.R.S.
- II. "The Propagation of Groups of Waves in Dispersive Media, with Application to Waves on Water produced by a Traveling Disturbance." By Dr. T. H. HAVELOCK. Communicated by Prof. J. LARMOR, Sec. R.S.
- III. "On the Refraction and Dispersion of Krypton and Xenon and their Relation to those of Helium and Argon." By C. CUTHBERTSON and M. CUTHBERTSON. Communicated by Prof. F. T. TROUTON, F.R.S.
- IV. "Note on Horizontal Receivers and Transmitters in Wireless Telegraphy." By Prof. H. M. MACDONALD, F.R.S.
- V. "On Optical Dispersion Formulæ." By Prof. R. C. MACLAURIN. Communicated by Prof. J. LARMOR, Sec. R.S.
- VI. "(i) On the Accumulation of Helium in Geological Time. (ii) On Helium in Saline Minerals and its Probable Connection with Potassium." By the Hon. R. J. STRUTT, F.R.S.\*
- VII. "Note on the Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum." By Prof. H. A. WILSON, F.R.S.
- VIII. "On Measurement of Rotatory Dispersive Power in the Visible and Ultra-violet Regions of the Spectrum." By Dr. T. MARTIN LOWRY. Communicated by Prof. H. E. ARMSTRONG, F.R.S.

\* Published during Autumn Recess.

November 26, 1908.

Dr. DAVID FERRIER, Vice-President, in the Chair.

His Grace the Duke of Bedford was admitted into the Society.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair, and the List of the Officers and Council for the ensuing year, proposed by the Council for election, was read as follows:—

*President.*—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., LL.D.

*Treasurer.*—Alfred Bray Kempe, M.A., D.C.L.

*Secretaries.*—{ Prof. Joseph Larmor, D.Sc., D.C.L., LL.D.  
{ Prof. John Rose Bradford, M.D., D.Sc.

*Foreign Secretary.*—Sir William Crookes, D.Sc.

*Other Members of the Council.*—Sir George Howard Darwin, K.C.B.; Prof. James Cossar Ewart, M.D.; Sir David Gill, K.C.B.; John Scott Haldane, M.D.; Charles Thomas Heycock, M.A.; Prof. Horace Lamb, D.Sc.; Prof. Hector Munro Macdonald, M.A.; Frederick Walker Mott, M.D.; the Hon. Charles Algernon Parsons, C.B.; Prof. William Henry Perkin, Ph.D.; Prof. Edward Bagnall Poulton, D.Sc.; Lieut.-Colonel David Prain, C.I.E.; Sir Arthur William Rücker, D.Sc.; Right Hon. Sir James Stirling, M.A.; Prof. Frederick Thomas Trouton, Sc.D.; William Whitaker, B.A.

The following papers were read:—

- I. "Some Experiments made to Test the Action of Extract of Adrenal Cortex." By S. G. SHATTOCK and C. G. SELIGMANN. Communicated by Prof. JOHN ROSE BRADFORD, For. Sec. R.S.
- II. "Further Results of the Experimental Treatment of Trypanosomiasis; being a Progress Report to a Committee of the Royal Society." By H. G. PLIMMER and Captain H. R. BATEMAN, R.A.M.C. Communicated by Prof. JOHN ROSE BRADFORD, For. Sec. R.S.
- III. "A Trypanosome from Zanzibar." By Colonel Sir DAVID BRUCE, C.B., F.R.S., and Captains A. E. HAMERTON, D.S.O., and H. R. BATEMAN.
- IV. "The Proportion of the Sexes produced by Whites and Coloured Peoples in Cuba." By W. HEAPE, F.R.S.
- V. "Further Researches on the Etiology of Endemic Goitre." By Captain R. MCCARRISON, I.M.S. Communicated by Major R. ROSS, C.B., F.R.S.

*November 30, 1908.*

**ANNIVERSARY MEETING.**

**Mr. A. B. KEMPE**, Vice-President and Treasurer, in the Chair.

The Report of the Auditors of the Treasurer's accounts was read, and the thanks of the Society were given to the Treasurer and to the Auditors.

The List of Fellows deceased and the List of Fellows elected into the Society since the last Anniversary were read.

The Report to the Society from the Council, upon the work during the past year, was, upon the motion of the Chairman, received.

The President's Address was read from the Chair.

On the motion of Sir William Huggins, seconded by the Earl of Berkeley, the thanks of the Society were voted to the President for his Address.

The Awards of the Medals for the year were announced as follows, and the Medals were presented from the Chair :—

The Copley Medal.....	To Dr. A. R. Wallace.
The Rumford Medal .....	„ Prof. H. A. Lorentz.
A Royal Medal .....	„ Dr. H. Head.
A Royal Medal .....	„ Prof. J. Milne.
The Davy Medal .....	„ Prof. W. A. Tilden.
The Darwin Medal .....	„ Prof. August Weismann.
The Hughes Medal .....	„ Prof. E. Goldstein.

The Chairman having, with the consent of the Society, nominated Dr. Hinde and Sir Joseph Swan as Scrutators, to assist the Secretaries in examining the balloting lists for the election of Council and Officers, the votes of the Fellows present were taken. The Scrutators reported that the Council and Officers nominated at the preceding meeting had been duly elected, and their names were accordingly announced from the Chair.

The thanks of the Society were given to the Scrutators.



The following Fellows were present and voted :—

A. W. Alcock.  
 H. E. Armstrong.  
 Lord Avebury.  
 W. Barlow.  
 A. B. Basset.  
 Earl of Berkeley.  
 T. G. Bonney.  
 F. D. Chattaway.  
 D. Clerk.  
 S. M. Copeman.  
 P. H. Cowell.  
 E. W. Creak.  
 Sir W. Crookes.  
 F. Darwin.  
 Sir G. H. Darwin.  
 A. Dendy.  
 W. H. Dines.  
 E. Divers.  
 A. M. W. Downing.  
 W. Duddell.  
 F. Elgar.  
 D. Ferrier.  
 A. M. Field.  
 M. O. Forster.  
 G. C. Foster.  
 W. Gardiner.  
 Sir A. Geikie.  
 F. D. Godman.  
 H. H. Godwin-Austen.  
 J. W. Gregory.  
 H. Head.  
 H. S. Hele-Shaw.  
 G. J. Hinde.  
 Sir W. Huggins.  
 T. McK. Hughes.  
 E. Hull.  
 G. W. Lamplugh.  
 J. Larmor.

C. H. Lees.  
 A. Liversidge.  
 Sir W. Macewen.  
 H. McLeod.  
 P. A. MacMahon.  
 Sir P. Manson.  
 J. E. Marr.  
 G. Matthey.  
 A. Muirhead.  
 G. H. F. Nuttall.  
 Hon. C. A. Parsons.  
 J. Perry.  
 W. J. Pope.  
 E. B. Poulton.  
 D. Prain.  
 C. Reid.  
 A. W. Reinold.  
 Sir A. W. Rücker.  
 Hon. B. Russell.  
 E. Saunders.  
 P. L. Sclater.  
 R. H. Scott.  
 W. N. Shaw.  
 O. Stapf.  
 Sir J. Stirling.  
 A. Strahan.  
 Sir J. W. Swan.  
 J. J. H. Teall.  
 Sir J. I. Thornycroft.  
 W. A. Tilden.  
 H. H. Turner.  
 V. H. Veley.  
 W. W. Watts.  
 W. Whitaker.  
 A. N. Whitehead.  
 Sir J. Wolfe Barry.  
 A. S. Woodward.  
 H. Woodward.

December 10, 1908.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

The Right Hon. Herbert Henry Asquith was admitted into the Society.

The President announced that he had appointed as Vice-Presidents :—

The Treasurer.  
Sir George Darwin.  
Prof. J. Cossar Ewart.  
Hon. C. A. Parsons.

The following Papers were read :—

- I. "Reciprocal Innervation of Antagonistic Muscles. XIIth Note : Proprioceptive Reflexes. XIIIth Note : On the Antagonism between Reflex Inhibition and Reflex Excitation." By Prof. C. S. SHERRINGTON, F.R.S.
- II. "Electrolytes and Colloids. The Physical State of Gluten." By Prof. T. B. WOOD and W. B. HARDY, F.R.S.
- III. "On the Specific Heats of Air and CO<sub>2</sub> at Atmospheric Pressure by the Continuous Electric Method at 20° and 100° C." By W. F. G. SWANN. Communicated by Prof. H. L. CALLENDAR, F.R.S.
- IV. "Potential Gradient in Glow Discharges from a Point to a Plane." By J. W. BISPHAM. Communicated by Prof. Sir J. J. THOMSON, F.R.S.
- V. "The Extension of Cracks in an Isotropic Material." By A. MALLOCK, F.R.S.
- VI. "Results of Magnetic Observations at Stations on the Coasts of the British Isles, 1907." By Commander L. CHETWYND, R.N. Communicated by Admiral A. M. FIELD, F.R.S.
- VII. "The Rotation of the Electric Arc in a Radial Magnetic Field." By J. NICOL. Communicated by Prof. H. A. WILSON, F.R.S.
- VIII. "On Anomalies in the Intensity in Diffracted Spectra." By Dr. H. C. POCKLINGTON, F.R.S.
- IX. "The Isothermal Layer of the Atmosphere and Atmospheric Radiation." By E. GOLD. Communicated by Dr. W. N. SHAW, F.R.S.
- X. "A Comparison of the Radium Emanation Spectra obtained by Different Observers." By T. ROYDS. Communicated by Prof. E. RUTHERFORD, F.R.S.

The Society adjourned over the Christmas recess to Thursday, January 14, 1909.



*June 4, 1908.*

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

Mr. John Stanley Gardiner and Mr. John Hilton Grace were admitted into the Society.

M. Henri Becquerel, Professor Friedrich Robert Helmert, Professor S. Kitasato, and Dr. Samuel Weir Mitchell were elected Foreign Members of the Society.

The following Papers were read :—

- I. "On the Aberration of Sloped Lenses, and on their Adaptation to Telescopes of Unequal Magnifying Power in Perpendicular Directions." By the LORD RAYLEIGH, O.M., Pres.R.S.
- II. "The Optical Constants of Gypsum at Different Temperatures, and the Mitscherlich Experiment." By Dr. A. E. H. TUTTON, F.R.S.
- III. "On the Viscosity of Ice." By R. M. DEELEY. Communicated by Dr. H. WOODWARD, F.R.S.
- IV. "The Effect of Temperature on the Neutralisation-volume Change for Different Salts at Different Concentrations." By Miss IDA FREUND. Communicated by F. H. NEVILLE, F.R.S.
- V. "Note on a New Sounding Machine for Use on Lakes and Rivers without a Boat." By Professor E. J. GARWOOD. Communicated by Professor T. G. BONNEY, F.R.S.
- VI. "The Electrical Qualities of Porcelain, with Special Reference to Dielectric Losses." By H. F. HAWORTH. Communicated by Professor W. E. AYRTON, F.R.S.
- VII. "On the Decay of the Radium Emanation when Dissolved in Water." By R. B. MOORE. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.

The Society adjourned over the Whitsun Recess to Thursday, June 18.

June 18, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

Professor Grafton Elliot Smith (elected 1907) was admitted into the Society.

The following Papers were read :—

- I. "An Electrical Method of Counting the Number of  $\alpha$  Particles from Radio-active Substances." By Professor E. RUTHERFORD, F.R.S., and Dr. HANS GEIGER.
  - II. "The Charge and Nature of the  $\alpha$  Particle." By Professor E. RUTHERFORD, F.R.S., and Dr. HANS GEIGER.
  - III. "On the Scattering of the  $\alpha$  Particles by Matter." By Dr. HANS GEIGER. Communicated by Professor RUTHERFORD, F.R.S.
  - IV. "Studies of the Processes operative in Solutions. Part VI.—Hydration, Hydrolation and Hydrolysis as Determinants of the Properties of Aqueous Solutions. VII.—The Relative Efficiencies of Acids as deduced from their Conductivities and Hydrolytic Activities. VIII.—The Influence of Salts on Hydrolysis, and the Determination of Hydration Values. IX.—The Determination of Optical Rotatory Power in Solutions. X.—The Changes effected by the Reciprocal Interference of Cane-sugar and other Substances (Salts and Non-electrolytes)." By Professor H. E. ARMSTRONG, F.R.S., and others.
  - V. "The Electrolytic Properties of Dilute Solutions of Sulphuric Acid." By W. C. D. WHETHAM, F.R.S., and H. H. PAINE.
  - VI. "The Giant Nerve Cells and Fibres of *Halla parthenopeia*." By Dr. J. H. ASHWORTH. Communicated by Professor J. C. EWART, F.R.S.
  - VII. "On Methods for the Continuous (Photographic) and Quasi-continuous Registration of the Diurnal Curve of the Temperature of the Animal Body." By Professor A. GAMGEE, F.R.S.
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*June 25, 1908.*

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "Have Trypanosomes an Ultra-microscopical Stage in their Life-History ?" By Colonel D. BRUCE, C.B., F.R.S., and Captain H. R. BATEMAN.
- II. "A Search for Possible New Members of the Inactive Series of Gases." (Introductory Note to the Papers by Mr. H. E. WATSON and Professor R. B. MOORE.) By Sir WILLIAM RAMSAY, K.C.B., F.R.S.
- III. "The Spectrum of the Lighter Constituents of the Atmosphere." By H. E. WATSON. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.
- IV. "An Investigation of the Heavier Constituents of the Atmosphere." By Professor R. B. MOORE. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.
- V. "On the Atomic Weight of Chlorine." By Dr. E. C. EDGAR. Communicated by Professor H. B. DIXON, F.R.S.
- VI. "Note on the Vapour Pressure and Osmotic Pressure of a Volatile Solute." By Professor H. L. CALLENDAR, F.R.S.
- VII. "Eutectics Research No. 1: Alloys of Lead and Tin." By W. ROSENHAIN and P. A. TUCKER. Communicated by Dr. R. T. GLAZEBROOK, F.R.S.
- VIII. "The Emission and Transmission of Röntgen Rays." By G. W. C. KAYE. Communicated by Professor J. J. THOMSON, F.R.S.
- IX. "Further Note on a Luminous Glow generated by Electrostatic Induction in an Exhausted Vessel made of Silica." By Rev. F. J. JERVIS-SMITH, F.R.S.
- X. "The Action of Chlorine upon Urea whereby a Dichloro Urea is produced." By Dr. F. D. CHATTAWAY, F.R.S.
- XI. "On the Reflection of Waves from a Stratum of Gradually Varying Properties, with Application to Sound." By Dr. J. W. NICHOLSON. Communicated by Professor J. LARMOR, Sec.R.S.

- XII. "Preliminary Account of the Habits and Structure of the Anaspidiidæ, with Remarks on some other Fresh-water Crustacea from Tasmania." By GEOFFREY W. SMITH. Communicated by Professor E. B. POULTON, F.R.S.
- XIII. "The  $\Omega$ -functions—a Class of Normal Functions." By E. CUNNINGHAM. Communicated by Professor K. PEARSON, F.R.S.
- XIV. "Diphtheria Antitoxin." By D. J. MELLANBY. Communicated by Professor J. N. LANGLEY, F.R.S.
- XV. "The Boiling-point of Sulphur on the Constant-pressure Air-thermometer." By N. EUMORFOPOULOS. Communicated by Professor CALLENDAR, F.R.S.
- XVI. "Note on the Boiling-point of Sulphur." By Professor H. L. CALLENDAR, F.R.S.
- XVII. "A Study of the Variations in the Secretion of Hydrochloric Acid in the Gastric Contents of Mice and Rats as compared with the Human Subject in Cancer." By Dr. S. M. COPEMAN, F.R.S., and Dr. H. W. HAKE.
- XVIII. "The Spectrum of Scandium and its Relation to Solar Spectra." By Professor A. FOWLER. Communicated by Sir W. CROOKES, F.R.S.
- XIX. "Note on the Instability of Tubes subjected to End Pressure, and on the Folds in a Flexible Material." By A. MALLOCK, F.R.S.

The Society adjourned over the Long Vacation to Thursday, November 5.

# PROCEEDINGS OF THE ROYAL SOCIETY.

SERIES A, VOL. 81, Appendix, 1908.

## OBITUARY NOTICES OF FELLOWS DECEASED.

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Illustrated by three photogravure portraits by Annan and Sons: the earlier one, p. xxxii, from a daguerreotype, represents Lord Kelvin about 1855, at the age of thirty; the middle one, p. lxiv, is from a negative by Fergus (now J. Stewart), of Largs, of date 1877; the later one, facing p. i, is from a negative by Dickinsons, New Bond Street, W., taken in 1907.	
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## WILLIAM THOMSON, LORD KELVIN.

Born in Belfast, June 26, 1824.  
Entered University of Glasgow, 1834.  
Entered at Peterhouse, Cambridge, October, 1841.  
B.A. and Fellow of Peterhouse, 1845.  
Professor of Natural Philosophy at Glasgow, 1846.  
Fellow of the Royal Society, 1851 ; Royal Medallist, 1856 ; Copley Medallist, 1883.  
Marriage to Miss Margaret Crum (deceased 1870), 1852.  
First Atlantic Cables laid, 1857-58.  
Permanent Atlantic Cables laid, 1865-66.  
Created a Knight, 1866 ; G.C.V.O., 1896.  
University of Glasgow removed to Gilmore Hill, 1870.  
President of the British Association, Edinburgh, 1871.  
Re-elected Fellow of Peterhouse, 1872.  
Marriage to Miss Frances Anna Blandy, 1874.  
Elected Foreign Associate Member of the Institute of France, 1877.  
Created Knight of the Prussian Order *Pour le Mérite*, 1884.  
Baltimore Lectures, 1884 ; enlarged edition, 1904.  
President of the Royal Society of Edinburgh, 1886-9 ; 1895-1907.  
Grand Officer of the Legion of Honour of France, 1890.  
Created a Peer of Great Britain, as Baron Kelvin of Largs, 1892.  
Jubilee Celebration, Glasgow, 1896.  
Retired from Glasgow Professorship, 1899.  
Order of Merit, original member, 1902.  
Privy Councillor of Great Britain, 1902.  
Chancellor of the University of Glasgow, 1904.  
Deceased December 17, buried in Westminster Abbey, December 23, 1907.

LL.D. (Cantab.), D.C.L. (Oxon.), Hon. Mem. Inst. Civ. Engin. ;—Foreign Member K. Preuss. Akad., Berlin ; K. Gesell. Wiss., Göttingen ; Soc. Ital. di Scienze, Milan ; R. Accad. d. Lincei, Rome ; K. Svenska Vetensk. Akad., Stockholm ; Kais. Akad. Wiss., Vienna ; Foreign Associate of the U.S. National Academy of Sciences, Washington ; etc., etc.

## WILLIAM THOMSON, BARON KELVIN OF LARGS. 1824—1907.

It would be impossible in an obituary of ordinary length to convey any idea of the many-sided activity by which Lord Kelvin was continually transforming physical knowledge, through more than two generations, more especially in the earlier period before practical engineering engrossed much of his attention in importunate problems which only he could solve. It is not until one tries to arrange his scattered work into the different years and periods, that the intensity of his creative force is fully realised, and some notion is acquired of what a happy strenuous career his must have been in early days, with new discoveries and new aspects of knowledge crowding in upon him faster than he could express them to the world.

The general impression left on one's mind by a connected survey of his work is overwhelming. The instinct of his own country and of the civilised world, in assigning to him a unique place among the intellectual forces of the last century, was not mistaken. Other men have been as great in some special department of physical science: no one since Newton—hardly even Faraday, whose limitation was in a sense his strength—has exerted such a masterful influence over its whole domain. He might have been a more learned mathematician or an expert chemist; but he would then probably have been a less effective discoverer. His power lay more in the direct scrutiny of physical activity, the immediate grasp of connecting principles and relations; each subject that he tackled was transformed by direct hints and analogies brought to bear from profound contemplation of the related domains of knowledge. In the first half of his life, fundamental results arrived in such volume as often to leave behind all chance of effective development. In the midst of such accumulations he became a bad expositor; it is only by tracing his activity up and down through its fragmentary published records, and thus obtaining a consecutive view of his occupation, that a just idea of the vistas continually opening upon him may be reached. Nowhere is the supremacy of intellect more impressively illustrated. One is at times almost tempted to wish that the electric cabling of the Atlantic, his popularly best known achievement, as it was one of the most strenuous, had never been undertaken by him; nor even, perhaps, the practical settlement of electric units and instruments and methods to which it led on, thus leaving the ground largely prepared for the modern refined electric transformation of general engineering. In the absence of such pressing and absorbing distractions, what might the world not have received during the years of his prime in new discoveries and explorations among the inner processes of nature.

His scientific papers, mostly mere fragments, which overflowed from his mind, as has been said, into the nearest channel of publication, have been collected by himself up to the year 1860, in somewhat desultory manner, in

four substantial volumes. In addition there are three volumes of Popular Lectures and Addresses, which are more finished products, perhaps equalled in weight and scope only by those of Helmholtz. His fertility, especially in the first dozen years from 1845 to 1856, seems to be almost without precedent. Owing to the want of systematic exposition, much of this progress was grasped only imperfectly by contemporaries, and even long afterwards; but the close attention of a few master minds, including Clerk Maxwell and in a less degree Helmholtz, and in certain respects that of the school of scientific electrical engineers that was rising into confident power under his own inspiration, made up partially for this failure. In the writings on Thermodynamics and the Theory of Available Energy, this lack of consecutive arrangement has remained until the present time a serious obstacle. In the notice\* of the first two volumes of the 'Collected Papers,' which was contributed to 'Nature' in 1885 by Helmholtz, the writer was so engrossed by this interesting episode as to devote nearly the whole review to its consideration; but even he has missed recognising that Thomson's 'dissipation of energy' was in 1855 determined quantitatively just as much as Clausius' 'entropy' was in the same month of the same year, and was, moreover, even then as wide in scope (*cf. infra*), making due allowance for the almost total absence of numerically exact physico-chemical data on which to develop it, as it had again become twenty years later in Helmholtz's own hands in 1882 or in those of Willard Gibbs in 1876-8.

Probably the severest ordeal to which a mass of occasional writings, evolving an entirely new range of thought, could be subjected, is that of republication after the lapse of years. The fragmentary character of the production of Thomson's papers, in scattered Journals and Transactions, naturally suggested ideas of obscurity to the workers who had time only to skim the content of separate papers without absorbing them as a connected whole; but it will probably be granted to be a most remarkable circumstance, and irrefragable proof of sureness of construction in a subject so difficult and entangled, that the papers on Thermodynamics, which also founded the modern general Theory of Energy, were capable of being reprinted in full with but slight occasional erasures, and those mainly of unessential character. Here one is, of course, leaving out of account the preliminary struggle to reconcile the apparently conflicting principles of Carnot and Joule, which forms one of the most instructive and fascinating episodes in scientific history.

We may be permitted to surmise that it was in the keen insight of these early years that his mental habitudes became fixed. His most striking characteristic all through life was insatiable thirst for knowledge, unwearied inquiry and investigation at all times, in season and out of season, combined with sympathetic interest and charming deference and encouragement to any person, however junior, who was honestly bent on the same pursuits. It is not surprising that, with new and profound views breaking in upon him from

\* 'Nature,' vol. 32 (1885), pp. 25-7; Helmholtz's 'Papers,' vol. 3, p. 593.

all sides, it should have grown into settled permanent habit that no mode of occupation of his time was to be allowed to interfere with the claims of scientific investigation.

Already when he took his degree at Cambridge in the Mathematical Tripos in January 1845, it appears that many subjects closely connected with fundamental advances of the ensuing time were fermenting in his mind. It was only a few months afterwards that he at length, after years of search, discovered for the scientific world Green's 'Essay on Electricity' of 1828, ever since one of the classics of mathematical physics; he obtained, in fact by accident, a copy from his previous mathematical tutor W. Hopkins, when he recognised how much of it he had anticipated by his own more intuitive results when still a boy. Soon afterwards he went to Paris to learn physical manipulation in the laboratory of Regnault—a fact which seems to have been forgotten when he recalled in graceful terms his obligations to the French science of his youth, in an address in connexion with the celebration of the centenary of the Institute of France, of which the echoes vibrated through Paris. He has put on record that, already even at that time, he went about among the Paris booksellers, inquiring for a copy of another work of genius, which he was himself to enroll among the few supreme classics of scientific knowledge, Sadi Carnot's small tract of 1824, 'Réflexions sur la Puissance Motrice du Feu;' he found in 1845 that it was quite forgotten, though they knew in the book-shops of the social and political writings of his brother, Hippolyte Carnot, ultimately his editor and biographer (1878) in later years.

WILLIAM THOMSON was eight years of age at the time of his father's transference to Glasgow from Belfast, in 1832, as Professor of Mathematics. Two years later he matriculated in that University, along with his elder brother James, at the age of ten, which was young even for the Scotland of that period; and recollections have survived of the eager part taken in his father's class by the small alert figure hardly out of childish costume. The date appended to his earliest scientific paper is Frankfort, July 1840, a year before he went, at the age of seventeen, as a student to Peterhouse, Cambridge, then, as since, a college with close Scottish connexions. It is stated that during the fortnight's visit to Germany, of which a record is thus attached to the paper, he read Fourier's Treatise on Heat, of 1822, with results that are conspicuous in this and in his other earlier papers which will presently be described. To the end of his life the work of Fourier, which for the first time rendered masses of rough observational data amenable to the resources of analysis, remained for him one of the classics of mathematical literature.

The period of his undergraduate career at Cambridge, extending from October 1841, to January 1845, when he graduated as second wrangler in the Mathematical Tripos but obtained the first of the Smith's Prizes, overflowed with original mathematical activity. The sketch given below of the notes and papers which he contributed to the 'Cambridge Mathematical Journal' during this time will show how high his thoughts were removed

from the didactic discipline which occupied, of necessity, the attention of the ordinary undergraduate; the main features of his subsequent mathematical interrogation of nature, the resolve not to lose himself under trains of symbolic calculations, but to draw out his analysis step by step in steady parallel with the ideas arising from direct interpretation of phenomena, are already conspicuous. Much of this habit of mind he must have taken with him from Glasgow, as the following sketch of the career of his father, a remarkable one on its own account, will perhaps show.

James Thomson the elder (1786–1849) supplies one of many cases that suggest problems as to the nature of the tendencies and faculties by which mathematicians are formed, often with very few apparent opportunities for development. He was fourth son\* of James Thomson, a farmer at Annaghmore, near Ballynahinch, a village in Co. Down, once of local repute as a health-resort or spa (the house of his birth was in 1898 known as Spamount), by his wife Agnes Nesbit. His early teaching was received solely from his father. Observing his bent for scientific pursuits, of which a re-invention of the principle of dialling is quoted as an example, his father sent him to an adjacent school at Ballykine, kept by Samuel Edgar, whose son attained eminence in the Irish Presbyterian Church. Here he soon rose to be an assistant. Wishing to become a minister in the Presbyterian Church, he entered Glasgow University in 1810, at the age of thirty-four, where he studied for several sessions, supporting himself by teaching at the school in the summer. In 1814, two years after graduating M.A. at Glasgow, he was appointed headmaster of the school of 'arithmetic, book-keeping, and geography' in the Academical Institution, Belfast, newly established by public contributions in what was then a small provincial town, yet very active both intellectually and politically; in 1815 he became Professor of Mathematics in its collegiate department.

He married, in 1817, Margaret (died 1830), eldest daughter of William Gardiner, of Glasgow, and had a family of four sons and three daughters, whose education he conducted with the utmost care; of the sons the eldest were James (1822–92) and William (1824–1907).

He published numerous text-books which were deservedly very successful:—'Arithmetic,' 1819, which, having been adopted by the Irish Education Department, has passed through nearly a hundred editions; 'Trigonometry, Plane and Spherical,' 1820; 'Modern Geography,' 1827; 'Differential and Integral Calculus,' 1831; 'Euclid,' with Appendix of Pure Geometry, 1834; 'Algebra,' 1844. On turning over the pages of some of these books again, the opinion is confirmed that in elegance and conciseness and choice of material, and knowledge of the classical mathematicians, they stand quite in the front rank of the text-books of that or any period. The University relations of their author seem, however, to have been solely with Glasgow, without direct contact either with Cambridge, where modern

\* These facts are taken largely from an article signed T. H. in the 'Dictionary of National Biography.'

mathematical methods had been introduced into the time-honoured curriculum by Herschel, Peacock, and Babbage about 1820, or with Dublin, which was always under French influences, and where a great native school was about to arise.

It is said that Lord Kelvin's elder brother, Professor James Thomson, undertook about 1890 a fundamental revision of the book on Arithmetic; but with characteristic passion for exactness, he became so involved in the preliminary epistemological ideas regarding the definition of number and magnitude, which more recently have amassed a large and abstruse literature of their own, that, to avoid a breakdown in health, the book had ultimately to be taken away from him by his brother and printed off.

The earliest of W. Thomson's contributions to the 'Cambridge Mathematical Journal' has two dates appended: Frankfort, July 1840, and Glasgow, April 1841. It is a defence of the accuracy of various expansions in trigonometrical series given in Fourier's 'Traité de la Chaleur,' which had been misunderstood by prominent writers. Another note on Fourier's work was published at the same time. Then followed an article "On the Linear Flow of Heat," Part I, November 1842, in which, discussing Fourier's solutions by definite integrals, he hits upon the observation that a given distribution of temperature does not in general represent a state of affairs that can have arisen from antecedents going back continuously into all past time; and in Part II, which followed in February 1843, he essays to answer the problem of the age of an assigned thermal distribution. He refers in the Reprint in 1881 to a paper published a year later for a clearer and more suitable discussion of this problem, which is, in fact, the procedure now natural for determining to what past time the convergency of the Fourier series subsists. Here, again recurring to his analogy with attractions (*infra*), he cannot resist appending a surmise that two attracting systems could not have the same field of force in a region outside them, which he is able to correct a year later still as a corollary to his famous discovery of the analytical method of image-systems.

At the same period he attended also to the now well-known theory of curvilinear isothermal co-ordinates, developed some years earlier by Lamé. His first note on this subject (May 1843) leads up, for two dimensions of space, to results now included under the applications of conjugate functions of a complex variable; and, after his custom, he drops a suggestion as to the considerable probability in favour of an extension of the theory to three dimensions. This is soon followed by a paper in which he investigates that question and withdraws his surmise; in it, by the Fourier method of flux, applied to a curvilinear element of volume, he leads directly to the characteristic equation of flow of heat in general co-ordinates, and thus replaces Lamé's own laborious analytical transformation.\* Here he is led

\* Jacobi's procedure for the same purpose by the Calculus of Variations is of date 1847, in his memoir on Laplace's Equation in 'Crelle,' vol. 37, or 'Werke,' vol. 2, pp. 191-216.

to the stream function for flux symmetrical around an axis, in which, as he remarks in the Reprint, he had been anticipated by Stokes in 1842. He returns to the original problem in November 1844, in connexion with a recent memoir by Lamé, which had given a complete solution, and also a note by Bertrand. A concise independent demonstration of Dupin's famous cognate theorem, that a triple system of mutually orthogonal surfaces intersect along their lines of curvature, forms the subject of another note.

About the same time he was already paying attention to a subject which, in its geodetic application, absorbed him much in later years, the theory of the steady configurations of revolving masses of homogeneous fluid. In November 1844, he publishes a proof of the result—obtained by the brief, direct, geometrical mode of argument in which he always delighted—that, provided the free surface of the fluid be an ellipsoid, whether it be one of Maclaurin's pair or that of Jacobi, the force of gravity must vary inversely as the distance of the tangent plane from the centre of the surface.

At the very time of his Mathematical Tripos and Smith's Prize Examinations, at Cambridge, he was preparing for press extensive papers on the Reduction of the General Equation of Surfaces of the Second Order and on the Lines of Curvature of such surfaces (Reprint, pp. 55–71).

It is hardly matter of wonder that the result of all this scientific activity of the highest order was that, in the Mathematical Tripos at the beginning of 1845, he only attained to the second place in the list. Two, at any rate, of the four examiners were men of mark, Robert Leslie Ellis and Harvey Goodwin. Inspection of the papers set by them, which were, on the whole, equal to their reputation, does not lend probability to the tale that some theorems taken from Thomson's published work were among the questions proposed, which, however, their author found himself unable to answer, though his rival (Stephen Parkinson, afterwards D.D., F.R.S., and Tutor of St. John's College) did not allow them to escape him.\* That the order of the result did not arise in any way from lack of appreciation is in accordance with the contemporary statement, that the examiners had given it out that they did not consider themselves worthy even to mend Thomson's pens. In the award of the Smith's Prizes immediately following, made by the mathematical professors under less restricted conditions, there could thus have been no room for so equivocal a result.

We now return to September 1841, when, at the age of seventeen, a

\* Another form of the tale is that in the Smith's Prize Examination two of the candidates answered a question in such striking and identical terms that investigation was made; when it turned out that the answers were taken from Thomson's path-breaking paper of four years previously, next to be referred to, which had appeared under his customary signature P. Q. R. As a fact, Earnshaw did set a question asking for a development of the general analogy between the theory of attractions and the conduction of heat.

Professor S. P. Thompson relates that, in answer to a question, Lord Kelvin recently told him that he deserved his defeat, owing to 'bad generalship' in spending too much time over problems that would not come out.

month before he entered at Peterhouse, he sent to the 'Cambridge Mathematical Journal' a paper "On the Uniform Motion of Heat in Homogeneous Solid Bodies, and its connexion with the Mathematical Theory of Electricity," doubtless another result of his study of Fourier's treatise mentioned above. By the time it was published, under the signature P. Q. R., in February 1842, he was able to prefix a note stating that, in the mathematical theorems reached, he had been largely anticipated by the great French mathematician Chasles. A further note to the reprint in 'Phil. Mag.,' 1854, relates the history of one of his great discoveries, this time a personal one. He there adds to his anticipators the name of Gauss, whose treatment of the subject had 'appeared shortly after Chasles' enunciations: and after all he found that these theorems had been discovered and published in the most complete and general manner, with rich applications to the theories of electricity and magnetism, more than ten years previously, by Green. It was not until early in 1845 that the author, after having inquired for it in vain for several years, in consequence of an obscure allusion to it in one of Murphy's papers, was fortunate enough to meet with a copy of the remarkable paper ('An Essay on the Application of Mathematical Analysis to the Theories of Electricity and Magnetism,' by George Green, Nottingham, 1828), in which this great advance in physical mathematics was first made. It is worth remarking that, referring to Green as the originator of the term, Murphy gives a mistaken definition of 'potential.' It appears highly probable that he may never have had access to Green's 'Essay' at all, and that this is the explanation of the fact (of which any other explanation is scarcely conceivable), that in his treatise on electricity (Murphy's 'Electricity,' Cambridge, 1833), he makes no allusion whatever to Green's discoveries, and gives a theory in no respect pushed beyond what had been done by Poisson. All the general theorems on attraction which Green, and the other writers referred to, demonstrated by various purely mathematical processes, are seen as axiomatic truths in approaching the subject by the way laid down in the paper which is now republished. The analogy with the conduction of heat, on which these views are founded, has not, so far as the author is aware, been noticed by any other writer."

The analysis in the part of this very remarkable paper in which he had been anticipated by Chasles and Gauss, retains its place almost unaltered in the text-books, to this day, as the classical and most compact method of treating such subjects as the attraction of ellipsoids and ellipsoidal shells;\* but more remarkable from a youth at the age of seventeen is the analogy, above referred to, between electric force and thermal flux, fundamentally illuminating to both, and pregnant with the great advances then impending in physical science.

The story of Thomson's discovery of George Green may now be completed from a footnote in the paper of 1845. "I should add that it was not till the beginning of the present year (1845) that I succeeded in meeting with

\* Cf., for instance, Thomson and Tait's 'Nat. Phil.'



Green's Essay. The allusion made to his name with reference to the word 'potential' ('*Mathematical Journal*,' vol. iii, p. 190) was taken from a memoir of Murphy's, 'On definite Integrals with Physical Applications,' in the '*Cambridge Transactions*,' where a mistaken definition of that term as used by Green is given." In 1850 he sent Green's 'Essay' to be reprinted in '*Crelle's Journal*,' vol. 39, with a prefatory notice, and it thenceforth assumed its place on the Continent as a classic: recently, in reply to inquiries about Green's biography, he wondered why he had not reprinted it in his own '*Cambridge Journal*.'

Early scientific impressions seem to have persisted with Thomson throughout life. To the end the names of Fourier and Green, whose fundamental importance he had been instrumental in elucidating in his own youthful work, remained for him among the very greatest in the scientific firmament.

We now pass on again to 1845; at the beginning of this year he had taken his degree, and then appeared before the public in his own name as the Editor of the '*Journal*.' He planned a series of papers "On the Mathematical Theory of Electricity in Equilibrium," the first of which appeared in November 1845, "On the Elementary Laws of Statical Electricity." The paper had been published in an earlier form in French in Liouville's '*Journal de Mathématiques*' about the middle of the year. In the course of it he already records incidentally the solution of the problem of the mutual influence of two charged spheres by his method of successive point-images. Yet the most interesting part of it is the end, where he applies himself to the elucidation of Faraday's physical views on electric induction. He points out that Faraday's idea of flux of induction involves precisely the analogy of electric force with flux of heat which he had himself developed in his earliest paper of 1841, the flow of heat being obviously conditioned, in accordance with Faraday's phrase, by the action of contiguous particles. He now remarks that Faraday's idea of polarisation of the particles of the dielectric medium is the exact analogue of Poisson's theory of induced magnetism, and (in the English edition of the paper) by reasoning on Poisson's principles he obtains the explanation of dielectric influence which holds good unchanged in electron-theory to this day;\* nor has it ever been better or more succinctly expressed. Curiously, though he expressly states that the effect becomes smaller as the molecules are fewer, yet his words seem to imply acceptance of the failure of Faraday's efforts with gases as evidence that the free molecules of a gaseous dielectric are not electrically polarisable. In a note to the '*Phil. Mag.*' Reprint of 1854, Thomson points out that this analogy of conductivity for heat is the precise equivalent of Faraday's "conducting power of a medium for lines of force"—a point of view which, however, was not reached by Faraday

\* The same theory of molecular polarisation was developed independently by Mossotti in the year following, '*Mem. della Soc. Italiana*,' vol. 24, as Thomson subsequently remarks; it is often connected with his name.

until five years later ('Exp. Res.,' Series 27, October 1850) as the expression of his experimental synthesis of the relations and properties of lines of magnetic force in iron and other highly magnetic media. Earlier, in 'Exp. Res.,' Series 11, of date November 1837, where the idea of curved lines of electrostatic induction is reached, it was the conception of tension along the lines and sideway pressure that had guided Faraday's thought.

The train of mathematical development of the ideas of Faraday, which was subsequently in Maxwell's hands to be moulded into our present theory of the phenomena of electricity and radiation, was begun in a short note which appeared early in 1847.\* Referring to the concluding paragraphs of the Eleventh Series of Faraday's 'Researches' (November 1837), with their dominant idea of induction along curved lines of force,† supposed to be transmitted essentially through interaction of contiguous particles, he states that this theory of Electrostatic Induction "suggests the idea that there may be a problem in the theory of elastic solids corresponding to every problem connected with the distribution of electricity on conductors, or with the forces of attraction and repulsion exercised by electrified bodies. The clue to a similar representation of magnetic and galvanic forces is afforded by Mr. Faraday's recent discovery (November 1845) of the affection with reference to polarised light of transparent solids subjected to magnetic or electromagnetic forces." Referring to Stokes' classical analysis of the Equilibrium of Elastic Bodies which had recently been published (1845), he points out that the states of strain that can persist freely in the interior of homogeneous elastic matter, under the appropriate surface forces and no internal ones, are those in which the displacement  $(\alpha, \beta, \gamma)$  satisfies the relation that  $\nabla^2 \alpha \cdot \delta x + \nabla^2 \beta \cdot \delta y + \nabla^2 \gamma \cdot \delta z$  is a perfect differential, say  $\delta \phi$ . He then restricts the discussion to the case of a medium incapable of compression.

In the special case  $\alpha \delta x + \beta \delta y + \gamma \delta z = -\delta r^{-1}$  of this relation,  $(\alpha, \beta, \gamma)$  coincides with the electric force due to unit charge at the origin, here represented (*e.g.*) by a small vesicle in the medium containing gas which exerts pressure in all directions.

In the next special case

$$\left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y}\right) \delta x + \left(\frac{\partial \gamma}{\partial x} - \frac{\partial \alpha}{\partial z}\right) \delta y + \left(\frac{\partial \alpha}{\partial y} - \frac{\partial \beta}{\partial x}\right) \delta z = -\delta \frac{lx + my + nz}{r^3},$$

\* 'Cambridge and Dublin Math. Journal,' vol. 2; 'Math. and Phys. Papers,' vol. 1, pp. 76-80; dated from Glasgow College, November 28, 1846.

† There will doubtless always be difference of opinion regarding the scope and definiteness of Faraday's idea of lines of force, which he used so effectively as a basis of geometrical reasoning about physical forces. That the elastic interaction here enunciated is not inconsistent with Faraday's own view appears from the following extract ('Exp. Res.,' No. 1304):—"I have used the phrases *lines of inductive force* and *curved lines of force* in a general sense only, just as we speak of the lines of magnetic force. The lines are imaginary, and the force in any part of them is the resultant of compound forces, every molecule being related to every other molecule in *all* directions by the tension and reaction of those which are contiguous." In his later magnetic work (1850) the language, however, suggests that the lines are to him more than mathematical representations.

the vector occurring on the left thus represents the *magnetic* force of a magnetic bipole situated at the origin and lying in the direction  $(l, m, n)$ ; it is expressed as the curl of the previous electric force  $(\alpha, \beta, \gamma)$ , that is, as twice the differential rotational displacement at the point considered.

Finally, if  $\alpha = -\frac{l}{r} + \frac{1}{2} \frac{\partial}{\partial x} \frac{lx + my + nz}{r}$ , with the related expressions for  $\beta$

and  $\gamma$ , the curl of  $(\alpha, \beta, \gamma)$  now represents the magnetic force due to a unit current-element situated at the origin along the direction  $(l, m, n)$ .

In these statements it is implied (already in 1847) that magnetic force is related to electric force as involving the differential rotation or curl of the latter. If he had probed the matter only a little further, he would have been forced to recognise, on Faraday's principles, that it is the time-gradient of the magnetic force that is so related; and the Maxwellian theory of the æther might have opened up to his view. But he winds up the brief and hurried note characteristically as follows:—"I should exceed my present limits were I to enter into a special examination of the states of a solid body representing various problems in electricity, magnetism, and galvanism, which must therefore be reserved for a future paper. *Glasgow College*, November 28, 1846." The future paper seems never to have arrived, but the present one was enough to give a lead to Maxwell's earliest studies.\*

It was in the previous year, November 1845, that Faraday communicated to the Royal Society what Lord Rayleigh has described as one of the finest of his discoveries, the detection of a relation connecting magnetism and light, in the circumstance that the plane of polarisation of light passing through matter is rotated by a magnetic field. One may safely assume that this result must have been deeply pondered over by Thomson: we are justified by the quotation, *supra*, in ascribing to its influence the idea underlying and pervading this note, that if electric force is represented by displacement of the particles of a medium the magnetic force is related to the resulting rotation (in Stokes' sense) of the differential element of volume.

After this great refusal to proceed, the subject of the underlying mechanism of electromagnetic phenomena goes out of sight for eleven years, until 1856.

This is a convenient place to refer to a note, of the end of the same year,† extending his solution (iii) above to elastic solids not incompressible: a displacement  $(\alpha, \beta, \gamma)$  of type given by  $\alpha = -g\frac{l}{r} + \frac{1}{2}f\frac{\partial}{\partial x} \frac{lx + my + nz}{r}$  represents the result of a force applied to an infinitely extended solid in the direction  $(l, m, n)$  at the origin of co-ordinates. He points out that general solutions may be developed by combining such "sources of strain" as he had combined

\* See in fact the reference to it in his first memoir "On Faraday's Lines of Force" (1856), in Maxwell's 'Scientific Papers,' vol. 1, p. 188; and repeatedly in the mechanical theory in "Physical Lines of Force," 'Phil. Mag.' 1861-2. The future paper did arrive in 1889, having been then written for 'Math. and Phys. Papers,' vol. 3; cf. *infra*, p. lxvii.

† 'Cambridge and Dublin Math. Journal,' vol. 3, p. 87.

sources of heat in his earlier paper,—a method succinctly and exhaustively exemplified by Stokes two years later in his memoir “On the Dynamical Theory of Diffraction,” and in fact utilised by Kirchhoff, Hertz, and all subsequent analysts in all domains of elastic theory.

Hitherto we have recounted work on the more physical side of electrical theory. Thomson’s early home training in Euclidean geometry shone conspicuously in his investigations on the distribution of electricity on spherical conductors. The beautiful and now familiar idea of electrical images was first published in Liouville’s ‘*Journal des Mathématiques*,’ in extracts from three letters to the editor, in October 1845, and in June 1846. The first of these extracts\* recalls conversations with Liouville on this subject in Paris, in 1845, whither Thomson had gone soon after taking his degree, in order to gain physical experience in Regnault’s laboratory. The second letter consists mainly of an exposition of the system of orthogonal co-ordinates (*cf. supra*, p. vii) in space, which is suitable for treating the problem of two spheres. A third letter of September 1846, states the result for the distribution of electricity on a thin spherical bowl: the analysis which led to it did not see the light until 1869, when it was published, with full numerical tables to illustrate electrostatic shielding, in ‘*Electrostatics and Magnetism*,’ pp. 178–191. The problem of the mutual influence of two electrified spheres was treated in full by the method of successive images, with numerical results calculated for a projected absolute electrometer on this principle, in ‘*Phil. Mag.*,’ 1853, and ‘*Electrostatics and Magnetism*,’ pp. 87–97. This method had been described to the British Association at Cambridge as early as 1845. The results relating to the mutual attraction of two equal spheres had been published (*supra*, p. x) in ‘*Cambridge and Dublin Math. Journal*’ the same year: it appears that the main parts of the investigation were communicated to Liouville by letter in 1849. Already in 1845 he deduced the force of attraction from the energy of the distribution, or “mechanical value,” as he called this function whose minimum property had attracted his attention as utilised in Gauss’ memoir of 1839; the function appeared for the first time as energy in Helmholtz’s ‘*Erhaltung der Kraft*’ in 1847, as he learned later.

His instant absorption of the contents of Green’s ‘*Essay*,’ and the rapid expansion of the method of images, are jointly illustrated by a note of October 1845 (when he was back in Peterhouse from Paris), in the ‘*Cambridge and Dublin Math. Journal*,’ in which he briefly indicates the application of this method to the determination of the induced magnetisation in a plate of soft iron, a problem of which the solution had been one of Green’s analytical *tours de force*. As is now well known, the problem for an infinite mass of iron with a plane face is solved by a single image; and he passes from this to a solution for a plate, which he proves to be identical with Green’s, by successive reflexions.

In Liouville’s ‘*Journal*,’ in 1847, reprinted in part in ‘*Cambridge and Dublin*

\* Reprint, ‘*Electrostatics and Magnetism*,’ p. 144.

*Math. Journal* early in 1848, he essays to demonstrate both the determinacy and the existence of the solution of the general differential equation of flux, thermal or electric, subject to appropriate conditions over a boundary. The method, reprinted in Thomson and Tait's '*Nat. Phil.*,' is to invent a volume integral of an essentially positive function, for which the characteristic equation of the flux is the condition of a stationary value as determined by the calculus of variations. As regards proof of the existence of a solution satisfying the conditions, this argument, employed also by Riemann in 1851, afterwards gave way, so far as the requirements of abstract analysis are concerned, and became discredited generally, through the destructive criticism of Weierstrass. It has doubtless been gratifying to believers in the policy of encouraging physical intuition as a mathematical resource, to learn that a recent improvement by Hilbert seems to have removed the difficulties.

Various less important analytical contributions to the '*Cambridge and Dublin Math. Journal*' need not be mentioned. The papers that have now been passed under review occupy 191 pages in the reprint on '*Electrostatics and Magnetism*,' and the first 112 pages of vol. 1 of the '*Mathematical and Physical Papers*.'

The activity of Thomson in connexion with the early British mathematical journals seems to demand special record. It has been seen that, beginning at seventeen years of age, he was an active supporter during his undergraduate days of the original '*Cambridge Math. Journal*.' Whatever was the cause, his contributions were all anonymous, being usually signed '*P. Q. R.*,' but in one case '*N. N.*' After he took his degree this journal gave place to the '*Cambridge and Dublin Math. Journal*,' and his first paper, of date October 14, 1845, appears under his name as "*W. Thomson, B.A., Fellow of St. Peter's College*," while the title-page of the first volume, of date 1846, gives his name as sole editor, with an additional description as Professor of Natural Philosophy in the University of Glasgow. The last volume of the previous series had appeared with the name of R. L. Ellis as editor. Thomson's connexion with the '*Journal*' continued until vol. 8, 1853; in this volume he was associated with N. M. Ferrers; the last volume, 9, was brought out, in 1853, by Ferrers alone. In 1857 the '*Quarterly Journal of Math.*' began its course, in order, as the editors expressed it, to enable English mathematicians to take their part in the rapid circulation and interchange of ideas. Its activity, which still continues, was then under the direction of J. J. Sylvester and N. M. Ferrers, assisted by G. G. Stokes, A. Cayley, and C. Hermite. Though the physical interest subsequently waned, the first number contains (pp. 57-77) a paper by W. Thomson, dated March 10, 1855, of fundamental importance in the then nascent general theory of energy, as will appear later.

The fact that the carrying on of the '*Journal*' for the eight years above described, with the editor so far from Cambridge as Glasgow, was a troublesome task, appears frequently in Thomson's correspondence with Stokes, in which he is often urging the necessity of getting material to enable an

impending part of the 'Journal' to be completed. The two friends exerted themselves to keep it going, and the 'Journal' has ever since retained its position as a classic, largely through their contributions in the domain of Mathematical Physics. In particular they planned a joint series of articles entitled "Notes on Hydrodynamics," designed for didactic purposes, which assisted conspicuously towards crystallising that subject into a formal science. The editor also pressed into the service his Scottish physical friends, such as Macquorn Rankine, and his brother James Thomson, who both made contributions of fundamental value—Rankine expounding the general theory of elasticity, including MacCullagh's rotational elasticity of the æther which he was the first to formulate in an objective way, while James Thomson treated, in most original manner, of the laws of spiral springs, and the influence of internal strain on the strength of materials, as well as the lowering of the freezing-point by pressure; and Dublin, in the persons of W. R. Hamilton, G. Salmon, S. Haughton, R. Townsend, and others, contributed her share.

The last of the notes on hydrodynamics, of February 1849,\* contains his theorem, that the motion of a fluid mass, arising from given movement impressed on its boundary, is the one involving the least possible energy: a proposition which, when extended in 1863 to any dynamical system† whatever, set in motion impulsively by imparting specified velocities, became fundamental in general dynamics under the name of Thomson's theorem.

As regards the contributions of Thomson and his friends, the 'Journal' fulfilled in the highest degree the main function of such a publication; everything was concise and pointed, and adapted to excite the interest of readers who were not specialists: there were few monographs. The reference in the admirable prefatory remarks introducing its successor, the 'Quarterly Journal,' and expressing the editors' sense of the heavy duties and responsibilities which it imposed, can easily be appreciated. "All who are interested in the cause of Mathematical Science are aware of the great and beneficial influence which has been brought to bear upon the study of Mathematics in this country by the publication of the 'Cambridge,' and subsequently of the 'Cambridge and Dublin Mathematical Journals,' which, if they cannot strictly be said to have created the present school of English mathematicians, may fairly claim to have provided the arena in which they have been able to measure their strength and give evidence of their capabilities. Causes upon the nature of which it is not necessary here to insist, having recently led to the discontinuance of the latter of these Journals, it became a question and a subject of anxiety among several of its former contributors and supporters how its place was to be supplied."

In November 1845, Faraday was able to communicate to the Royal Society the successful issue of long-continued efforts to find a connexion between

\* 'Math. and Phys. Papers,' vol. 1, p. 107.

† 'Thomson and Tait,' § 312.

light and electricity. This was the brilliant detection of the rotation of the plane of polarisation of light passing through material bodies by a magnetic field, which formed the beginning of a fresh series of discoveries relating to the magnetic state in all kinds of matter; and he pointed out its distinction from the intrinsic rotation produced (*e.g.*) by passage through quartz or sugar solution.

Thomson, in May 1856,\* probed the underlying dynamical meaning of this difference. The result is emphasised, that the existence of structural rotation is inconsistent with complete homogeneity of the transmitting medium, and points to its containing molecular elements, which must be of essentially spiral quality, due either to spiral crystalline arrangement of non-spiral molecules as in quartz, or to molecules each structurally spiral as in active liquids. The introductory paragraphs, which were fateful in the history of electrical science, are here quoted. Maxwell, in his 'Treatise' (1872, § 831), reproduces the second paragraph as an "exceedingly important remark" or argument on which the whole subject of the relation of light to magnetism must be based.

"The elastic reaction of a homogeneously strained solid has a character essentially devoid of all helicoidal and of all dipolar asymmetry. Hence the rotation of the plane of polarisation of light passing through bodies which either intrinsically possess the helicoidal property (syrup, oil of turpentine, quartz crystals, etc.), or have the magnetic property induced in them, must be due to elastic reactions dependent on the heterogeneousness of the strain through the space of a wave, or to some heterogeneousness of the luminous motions† dependent on a heterogeneousness of parts of the matter of lineal dimensions not infinitely small in comparison with the wave-length. An infinitely homogeneous solid could not possess either of those properties if the stress at any point of it was influenced only by parts of the body touching it; but if the stress at one point is directly influenced by the strain in parts at distances from it finite in comparison with the wave-length, the helicoidal property might exist, and the rotation of the plane of polarisation, such as is observed in many liquids and in quartz crystals, could be explained as a direct dynamical consequence of the statical elastic reaction called into play by such a strain as exists in a wave of polarised light. It may, however, be considered more probable that the matter of transparent bodies is really heterogeneous from one part to another of lineal dimensions not infinitely small in comparison with a wave-length, than that it is infinitely homogeneous and has the property of exerting finite direct 'molecular' force at distances comparable with the wave-length, and it is certain that any spiral heterogeneousness of a vibrating medium must, if either right-handed or left-handed spirals predominate, cause a finite

\* 'Roy. Soc. Proc.' vol. 8, pp. 150-8; 'Baltimore Lectures,' Appendix F.

† "As would be were there different sets of vibrating particles, or were Rankine's important hypothesis true, that the vibrations of luminiferous particles are directly affected by pressure of a surrounding medium in virtue of its inertia."

rotation of the plane of polarisation of all waves of which lengths are not infinitely great multiples of the steps of the structural spirals. Thus a liquid filled homogeneously with spiral fibres, or a solid with spiral passages through it of steps not less than the forty-millionth of an inch, or a crystal with a right-handed or a left-handed geometrical arrangement of parts of some such lineal dimensions as the forty-millionth of an inch, might be certainly expected to cause either a right-handed or a left-handed rotation of ordinary light (the wave-length being  $1/40000$  of an inch for homogeneous yellow).

"But the magnetic influence on light discovered by Faraday depends on the direction of motion of moving particles. For instance, in a medium possessing it, particles in a straight line parallel to the lines of magnetic force, displaced to a helix round this line as axis, and then projected tangentially with such velocities as to describe circles, will have different velocities according as their motions are round in one direction (the same as the nominal direction of the galvanic current in the magnetising coil), or in the contrary direction. But the elastic reaction of the medium must be the same for the same displacements, whatever be the velocities and direction of the particles; that is to say, the forces which are balanced by centrifugal force of the circular motions are equal, while the luminiferous motions are unequal. The absolute circular motions being, therefore, either equal or such as to transmit equal centrifugal forces to the particles initially considered, it follows that the luminiferous motions are only components of the whole motion, and that a less luminiferous component in one direction, compounded with a motion existing in the medium when transmitting no light, gives an equal resultant to that of a greater luminiferous motion in the contrary direction compounded with the same non-luminous motion. I think it is not only impossible to conceive any other than this dynamical explanation of the fact that circularly polarised light transmitted through magnetised glass parallel to the lines of magnetising force, with the same quality, right-handed always, or left-handed always, is propagated at different rates according as its course is in the direction or is contrary to the direction in which a north magnetic pole is drawn, but I believe it can be demonstrated that no other explanation of that fact is possible. Hence it appears that Faraday's optical discovery affords a demonstration of the reality of Ampère's explanation of the ultimate nature of magnetism, and gives a definition of magnetisation in the dynamical theory of heat. The introduction of the principle of moments of momenta ('the conservation of areas') into the mechanical treatment of Mr. Rankine's hypothesis of 'molecular vortices,' appears to indicate a line perpendicular to the plane of resultant rotatory momentum ('the invariable plane') of the thermal motions as the magnetic axis of a magnetised body, and suggests the resultant moment of momenta of these motions as the definite measure of the 'magnetic moment.' The explanation of all phenomena of electromagnetic attraction or repulsion, and of electromagnetic induction, is to be looked for simply in the inertia and



pressure of the matter of which the motions constitute heat. Whether this matter is or is not electricity, whether it is a continuous fluid inter-permeating the spaces between molecular nuclei, or is itself molecularly grouped, or whether all matter is continuous, and molecular heterogeneousness consists in finite vortical or other relative motions of contiguous parts of a body, it is impossible to decide, and, perhaps, in vain to speculate, in the present state of science.

"I append the solution of a dynamical problem for the sake of the illustrations it suggests for the two kinds of effect on the plane of polarisation referred to above."

After some dynamical gyrostatic effects of cognate character have been discussed by mathematical analysis, the paper ends by a paragraph as follows:—"From these illustrations it is easy to see, in an infinite variety of ways, how to make structures, homogeneous when considered on a large enough scale, which (1) with certain rotatory motions of component parts having, in portions large enough to be sensibly homogeneous, resultant axes of momenta arranged like lines of magnetic force, *shall have the dynamical property by which the optical phenomena of transparent bodies in the magnetic field are explained*; (2) with spiral arrangements of component parts, having axes all ranged parallel to a fixed line, *shall have the axial rotatory property corresponding to that of quartz crystal*; and (3) with spiral arrangements of component groups, having axes totally unarranged, *shall have the isotropic rotatory property possessed by solutions of sugar and tartaric acid, by oil of turpentine, and many other liquids.*"

He returns incidentally to the subject,\* insisting that "electrodynamic capacity" is "identical in meaning with the 'simple mass-equivalent' in the motion of Attwood's machine as ordinarily treated." This "it seems quite certain must be owing to true inertia of motions accompanying the current, chiefly rotatory, with axes coinciding with the lines of magnetic force in the iron, air, or other matter in the neighbourhood of the conductor, and continuing unchanged so long as the current is kept unchanged."

It may be recalled that it was in 1858 that the dynamical theory of vortex motion in fluids was created by the great memoir of Helmholtz ('Crelle's Journal,' vol. 55). Maxwell, in his 'Treatise,' § 822, improving upon a section in his memoir "On Physical Lines of Force," of 1862, used all the data available to connect the propagation of light with the magnetism, on the basis that the magnetic force is a vortical molecular phenomenon in the medium which combines in a scalar manner with the vortical quality in the motion that constitutes radiation, as regards the energy function which determines the dynamics, and also that the magnetic field alters by the light-motion as vortices in fluid would do. He finds that this hypothesis is the same thing, as regards continuous propagation, as a scalar connexion between the motion of the medium and the total electric current which is the equivalent of the magnetism. The more recent observations, however, connect the optical effect

\* 'Roy. Soc. Proc.,' vol. 11, 1861, footnotes p. 273.

with the magnetisation instead of the magnetic force, as modern molecular theory would indicate.

At the beginning of the same year 1856, near the end of the twenty-fourth year of his age, and two years after taking his degree at Cambridge, James Clerk Maxwell communicated to the Cambridge Philosophical Society his earliest electrical memoir, "On Faraday's Lines of Force." His genius was as systematic as Thomson's was desultory. This paper, and the subsequent one "On Physical Lines of Force," in the '*Philosophical Magazine*' for 1861, were as much an exposition of Thomson's interpretations as the former was also of Faraday's own views. A study of the general sketches prefixed to these papers would be, in fact, one of the best ways of appreciating the extent of Thomson's activity in electrical theory up to that date. Nothing that Maxwell wrote is more illuminating than these preliminary essays on the scope of scientific explanation, and the enforcement, from the examples of Faraday and Thomson, of the effective superiority of graphic and plastic analogical reasoning over self-centred abstract calculations. When he passes on to try to fit together the various partial aspects of the electrical theory into a single connected scheme, the lucidity of the previous general sketch deserts him, as might be expected from the difficulty of the enterprise; though the defect is possibly in part due to over-elaboration of the analytical apparatus, which could have been better grasped as a whole if more condensed. The same fault attaches in a greater degree to the treatise on '*Electricity and Magnetism*,' made up as it seems of a series of partial preliminary sketches, intended to be welded ultimately into a systematic treatise, but which he appears to have been induced to throw into the press on his coming to Cambridge in 1871, in order to supply the urgent need of some accessible exposition of the new physical views for the use of students. A remark of his has been handed down which points in this direction—to the effect that the aim of his book was not to finally expound the theory for the world, but to educate himself by the presentation of a view of the stage he had reached. This would, at any rate, account for the disjointed character of the '*Treatise*,' and the sudden transitions in the points of view between different chapters, which have been found to be so puzzling and have naturally induced remonstrance from readers unacquainted with the evolution of the subject. Instead of tying himself down to a definite ordered exposition, with all material which cannot be fitted into it rejected as irrelevant or unprofitable, the aim is purposely to keep the subject open, to record all the converging considerations and lines of argument that have a chance of proving useful or suggestive for the ultimate unification. Much misunderstanding has thereby been caused both in this country and abroad, and many complaints of the absence of logical cohesion; not a few reconstructions have been offered by stringing together excerpts so as to make one consecutive story, filling in the gaps according to predilection, but ignoring the remaining aspects as mere disturbances of the train of explanation. And for didactic purposes this has

doubtless been a help; though we may agree with Boltzmann that it could hardly be done better than Maxwell did it himself, in the introductory expositions prefixed to his earlier papers; or, later, in an appendix to his memoir ('Phil. Trans.,' 1868) on the ratio of the electric units, where he sets forth a skeleton of the theory of light, of the approved modern heuristic pattern, in order to meet a demand for a concise conspectus of its content. It is noteworthy that Maxwell's general argument there for the existence of a transmitting medium is precisely that, without support from an æther, the forces between electric bodies cannot be arranged, on any existing theory, so as to form a balance, as regards either momentum or energy—that without it reaction does not balance action and the energy is not conserved.

In the final instalment of the paper "On Physical Lines of Force," 'Phil. Mag.,' February 1862, Maxwell emphasises Thomson's demonstration, quoted above, that magnetism involves essentially the rotational motion of something around its lines of force. He probes and develops tentatively a theory of the magnetic force as due to the centrifugal force of vortices associated with the molecules of matter, assuming that these vortices "consist of the same matter the vibrations of which constitute light." But directly afterwards\* he seems almost to repent of this unnecessary restriction, under the fascination of Weber's theory of moving electric particles:—"I am inclined to believe that iron differs from other substances in the manner of its action as well as in the intensity of its magnetism; and I think this behaviour may be explained on our hypothesis of molecular vortices, by supposing that the particles of the *iron itself* are set in rotation by the tangential motion of the vortices, in an opposite direction to their own. These large heavy particles would thus be revolving exactly as we have supposed the infinitely small particles constituting electricity to revolve, but without being free like them to change their place and form currents." Knowledge has crystallised since this remarkable passage was written: the "infinitely small particles constituting electricity" have undergone a natural evolution from Weber's attracting particles into the electrons appropriate to Maxwell's theory: it is *their* rotation in the molecule that conditions the magnetic phenomena: and Maxwell's notion of a molecular aggregate in iron rotating as a whole may yet be a clue to the explanation of ferromagnetics. His analytical development, however, is difficult to interpret on either view. In the "Dynamical Theory," 'Phil. Trans.,' 1864, he harks back (§ 8) to the idea of rotation of the æther: the time was not yet ripe for the electrons as the originators of the disturbances whose propagation he studied so closely.

It seems that it was not until 1864 that Maxwell had reached the electric theory of light, these studies in the Faraday magneto-optic relation, even as reproduced in modified form in the 'Treatise,' being purely tentative and provocative of the deeper plunge. Thus, writing in 1864, "the conception of the propagation of transverse magnetic disturbances to the exclusion of normal ones is distinctly set forth by Professor Faraday in his 'Thoughts on

\* 'Scientific Papers,' vol. 1, p. 507.

Ray Vibrations,' 'Phil. Mag.,' 1864. The electromagnetic theory of light, as proposed by him, is the same in substance as that which I have begun to develop in this paper, except that in 1846 there were no data to calculate the velocity of propagation."\* Maxwell did not return to the subject, but left the application to the laws of optical reflexion and dispersion to be developed by others, Helmholtz, FitzGerald, etc.; some of the reasons why he did not consider the detailed optical theory for material bodies to be quite ripe for treatment appear from his correspondence with Stokes, recently published.†

This is the suitable place to insert a summing up of his own ideas on this subject by Thomson, made just before Maxwell began his attack on the physical side of the problem of the æther. It forms the peroration to an eloquent discourse on atmospheric electricity, delivered at the Royal Institution, May 18, 1860.‡

"The speaker could not conclude without guarding himself against any imputation of having assumed the existence of two electric fluids or substances, because he had frequently spoken of the vitreous and resinous electricities. Dufay's very important discovery of two modes or qualities of electrification led his followers too readily to admit his supposition of two distinct electric fluids. Franklin, Æpinus, and Cavendish, with a hypothesis of one electric fluid, opened the way for a juster appreciation of the *unity* of nature in electric phenomena. Beccaria, with his 'electric atmospheres,' somewhat vaguely struggled to see deeper into the working of electric force, but his views found little acceptance, and scarcely suggested inquiry or even meditation. The eighteenth century made a school of science for itself, in which, for the not unnatural dogma of the earlier schoolmen, 'matter cannot act where it is not,' was substituted the most fantastic of paradoxes, *contact does not exist*. Boscovich's theory was the consummation of the eighteenth century school of physical science. This strange idea took deep root, and from it grew up a barren tree, exhausting the soil and overshadowing the whole field of molecular investigation, on which so much unavailing labour was spent by the great mathematicians of the early part of our nineteenth century.§ If Boscovich's theory no longer cumbers the ground, it is because one true philosopher required more light for tracing lines of electric force.

"Mr. Faraday's investigation of electrostatic induction influences now every department of physical speculation, and constitutes an era in science. If we can no longer regard electric and magnetic fluids attracting or repelling at a distance as realities, we may now also contemplate as a thing of the past that belief in atoms and in vacuum, against which Leibnitz so earnestly contended in his memorable correspondence with Dr. Samuel Clarke.

\* 'Dynamical Theory of the Electromagnetic Field,' October, 1864, § 20.

† 'Sir G. G. Stokes, Memoir and Scientific Correspondence,' vol. 2, pp. 1-45.

‡ 'Electrostatics and Magnetism,' p. 223, §§ 288-291.

§ In later years Lord Kelvin would have partially withdrawn this, finding it still necessary to form hypotheses about the field of force of an atom in the absence of knowledge of what the atom itself intrinsically consists of. Cf. 'Baltimore Lectures, 2 ed., 1904.

"We now look on space as full. We know that light is propagated like sound through pressure and motion. We know that there is no substance of caloric,—that inscrutably minute motions cause the expansion which the thermometer marks, and stimulate our sensation of heat,—that fire is not laid up in coal more than in this Leyden phial, or this weight, there is potential fire in each. If electric force depends on a residual *surface action*, a resultant of an inner tension experienced by the insulating medium, we can conceive that electricity itself is to be understood as not an accident, but an essence of matter. Whatever electricity is, it seems quite certain that electricity in motion is *heat* ;\* and that a certain alignment of axes of revolution in this motion is *magnetism*. Faraday's magneto-optic experiment makes this not a hypothesis, but a demonstrated conclusion. Thus a rifle bullet keeps its point foremost; Foucault's gyroscope finds the earth's axis of palpable rotation; and the magnetic needle shows that more subtle rotatory movement in matter of the earth, which we call terrestrial magnetism—all by one and the same dynamical action.

"It is often asked, are we to fall back on facts and phenomena, and give up all idea of penetrating that mystery which hangs round the ultimate nature of matter? This is a question that must be answered by the metaphysician, and it does not belong to the domain of Natural Philosophy. But it does seem that the marvellous train of discovery, unparalleled in the history of experimental science, which the last years of the world has seen to emanate from experiments within these walls, must lead to a stage of knowledge, in which laws of inorganic nature will be understood in this sense that one will be known as essentially connected with all, and in which unity of plan through an inexhaustibly varied execution will be recognised as a universally manifested result of creative wisdom."

His studies in the doctrine of energy (*infra*, p. xxix) soon led Thomson into the intricate problem of the mechanical value of an electric current (*i.e.*, the *electrokinetic* energy), through which he successfully threaded his way. What he published is a brief statement in Nichol's 'Cyclopædia,' edition 1860, "Magnetism, Dynamical Relations of." He explains that the inertia concerned cannot be intrinsic inertia of the moving electricity, for Faraday found that a current doubled back on itself gave no sensible spark on breaking the circuit; yet, if such inertia were ever detected it could readily be included. It is the energy of the electric induction to which the inertia belongs, as Faraday himself recognised. He sees that when two currents, each sustained constant by an impressed electromotive force, are allowed to develop energy of mechanical work by their mutual attraction, their electrokinetic energy is also increased by an equal amount, both these amounts being provided from the energy of the battery. Thus, for example, the

\* This view has been curiously revived in some recent theories of electric and thermal conduction.

electrokinetic energy of a single circuit is the work that would have to be *done* to double it close upon itself.\* He states that this energy is the volume integral throughout space of square of magnetic force divided by  $8\pi$ ; an expression which Maxwell took later, with happy results, to represent the electrokinetic energy in distribution as well as in amount. In 'Elec. and Mag.,' 1872, p. 447, where this statement is reprinted in full in a footnote, he adds a most interesting memorandum of date October 13, 1851, which shows how he had teased it into form. He had thought "that the [mechanical] value of a current will be affected by steel [*i.e.*, permanent] magnets in its neighbourhood." But he was shaken in this by Faraday's having found that soft iron is better than steel. He "made out the true state of the case," which was that when a current is moved near a permanent magnet the gains and losses of energy compensate without demanding any alteration in its intrinsic energy due to change of its position. But when one maintained current is moved near another, the principle of conservation of total energy, electrical and thermal, requires that their electrokinetic energy shall *increase* by the mechanical work they perform in their change of position.

This verification of the conservation of the total energy (October 1851) belongs to the time when Thomson had finally given his adhesion to Joule's doctrine that heat is energy instead of being a substance, and the development of thermodynamics was in full cry. Unknown to him, the same problem had been essayed in a tract which formed one of the highest efforts of genius applied to the development of the Theory of Energy, the famous 'Erhaltung der Kraft' of Helmholtz, published by him in 1847 to meet, as he said afterwards, with neglect from contemporary physicists (yet F. E. Neumann was then in his prime), redeemed, however, by the educated appreciation of the great mathematician Jacobi. Helmholtz had not then been under Faraday's influence, and could have no idea of energy stored in organised kinetic form in the magnetic field of the current; accordingly, when he puts down the equation of conservation for two mutually influencing currents, he gets it wrong.† For the case of a current and a permanent magnet it comes right, but it required Thomson's examination to prove that it is so.‡ Thus to Helmholtz belongs the merit of determining theoretically the constant of proportionality in Faraday's law of induction, by the aid of the conservation of energy: while Thomson's closer examination brought to light that the one equation of energy could determine only one variable, and thus prepared the way for Maxwell's application of the generalised dynamics of Lagrange,

\* This had been published in 'Proc. Glasgow Phil. Soc.,' January 1853. Cf. 'Math. and Phys. Papers,' vol. 1, p. 530.

† It was so quoted in Maxwell's 'Treatise,' vol. 2, § 544 (1872). It remains so in the reprint, Helmholtz's 'Abhandlungen,' vol. 1, p. 64 (1881); but in pp. 91-5 are some improvements of date 1854 as regards induction with magnetisable iron that were called forth by the criticism of Clausius.

‡ Cf., however, Helmholtz's addition of 1854 in reply to Clausius, where he mentions his difficulty of access to electrical literature in 1847, and modestly places the chief merit of the essay in the point of view.

which came only in 1864.\* Thomson had, however, as early as 1848, communicated to the British Association† an investigation based on Neumann's expression for the law of induction, and on the same lines as Helmholtz's exposition; he there speaks of  $ki^2$  as "mechanical effect continually lost or spent in some physical agency (according to Joule, the generation of heat)."

Thomson was not slow in developing the entrance to the mechanical relations of electric currents, and of electric inertia, thus obtained. The classical paper on transient currents was communicated to the Glasgow Phil. Soc. in January 1853,‡ and published in full in the 'Phil. Mag.' the following June. It contains the demonstration that oscillatory electric discharges must exist under suitable circumstances,—and gives that determination of their period which, in the hands of Hertz, led to the detection of electric waves in free space, bringing with them wireless telegraphy, and in the other direction nearly bridging the gap between electric experiments and optical phenomena. It appears from a footnote (p. 549) that he arrived at this theory early in 1852. He afterwards found that Helmholtz had definitely suspected the oscillatory character of the discharge, in the 'Erhaltung der Kraft' (1847), from its alternating effects in magnetisation as observed by Riess, and from the evolution of mixed gases in electrolysis which was discovered by Wollaston and at a later time puzzled Faraday.

We now pass to another phase of Thomson's mental activity. His first formal memoir—'in the grand style' as has been said—appeared§ in 1849, on "The Mathematical Theory of Magnetism." As he recounts in an abstract, in the magnetic theory of Poisson, employed by Green and by Murphy, the development is based on a hypothesis of two magnetic fluids, which the recent discoveries in electromagnetism had rendered incongruous. The aim of the memoir is to purify the expression of the theory by placing the results on a wider foundation. The general idea of polarity and of a polar element of volume is defined and made precise. "However different are the physical circumstances of magnetic and electric polarity, it appears that the positive laws of the phenomena are the same,|| and therefore the mathematical theories are identical. Either subject might be taken as an example of a very important branch of physical mathematics which might be called 'A Mathematical Theory of Polar Forces.'" The memoir proceeds with abundant explanation, perhaps needed at that time to supplant the cruder imagery, and to enforce the relation of Poisson's ideal density of magnetic matter to the actual distribution of polarity which it, only in certain respects, represents. He defines the *potential*, with due reference to Green's intro-

\* 'Dynamical Theory . . .,' §§ 17, 24 *seq.*

† 'Math. and Phys. Papers,' vol. 1, p. 81.

‡ 'Math. and Phys. Papers,' vol. 1, p. 534.

§ 'Transactions of the Royal Society' for June 1849, and June 1850.

|| Referring for this to 'Cambridge and Dublin Math. Journal,' vol. 1, 1845, as *supra*.

duction of the name in 1828, and shows that if that function is calculated as for the distribution of ideal magnetic matter, its gradient represents the magnetic force, defined as Maxwell used the term afterwards, to represent the force in a cavity of such elongated shape in the polarised medium that there is no sensible purely local part. In the Reprint in 1871 is here inserted, in illustration, an investigation of the centre and axes of a magnet, reproduced in Maxwell's Treatise (§ 392 *seq.*) the following year. Then the *mutual potential energy* of two magnets is formulated with a view to the determination of their attractions. A chapter follows on solenoidal and lamellar distributions of magnetism, and as a special case the Gaussian magnetic shell, which perhaps may be said to have expressed a theory of Ampère in the new geometrical terminology of solid angles. Then follow long disquisitions, partly interpolated in the Reprint from contemporary manuscripts, partly of date 1871, which confirm the impression that the writer's strength does not lie in synthetic exposition, but rather in flashes of insight and play of suggestion around his results such as have already been passed in review.

A footnote of 1872 explains that in 1850 he had no belief\* in the reality of Ampère's theory of magnetism, not then knowing "that motion is the very essence of what has been hitherto called matter. At the 1847 Meeting of the British Association at Oxford, I learned from Joule the dynamical theory of heat, and was forced to abandon at once many, and gradually from year to year all other, statical preconceptions† regarding the ultimate causes of apparently statical phenomena." Then the introduction to his paper of 1856 on the dynamics of magneto-optics is quoted in full as already reproduced (*supra*, p. xvi).

At the end of the Reprint he inserts a paper, "On the Potential of a Closed Galvanic Circuit of any Form," of date 1850,‡ which, besides emphasising the energy-aspect of the potential, is concerned with definitions (suggested by some of De Morgan's on area) of solid angle for complex convoluted types of circuits, which is in fact a subject in *Analysis Situs*.

It will be convenient to follow out here the more recent additions on magnetic theory which make up the remainder of the Reprint. There is a chapter on the Mechanical Value (Energy) of Distributions of Matter and of Magnetism. Then follows a chapter on "Hydrokinetic Analogy" to Magnetic Flux, and a further paper at the end entitled "General Hydrokinetic Analogy for Induced Magnetism" (1872), which are in fact extensions of the beautiful representation by frictionally resisted flow through a solid porous mass, which Maxwell had employed, apparently unknown to him, with much elegance in his earliest memoir "On Faraday's Lines of Force." In the latter paper the new term 'permeability' (to flux) is defined as an equivalent for coefficient of induction.

\* "It is absolutely impossible to conceive of the currents which he (Ampère) describes, round the molecules of matter, as having a physical existence," 'Brit. Assoc.' 1867 (Oxford); 'Elec. and Mag.', p. 469.

† His first memoirs on vortex motion are of date 1867-9.

‡ 'Cambridge and Dublin Math. Journal.'



A chapter on 'Inverse Problems' in Magnetism is added, containing much detail on the analogy with flow, after the manner of his first paper of 1845. Here a characteristic passage is of personal interest. "With reference to these problems I find a leaf of manuscript written in French, indorsed:— 'Fragment of draft of letter to M. Liouville, written on the Faulhorn, Sunday, September 12, 1847, and posted on the Monday or Tuesday week after, at Maidstone. The letter has not been published yet, although in September 1848, I understood from M. Liouville, in Paris, that he had it for publication. Probably it has fallen aside and is lost [?in consequence of the disturbed state of Paris at that time], which I should regret, as it contains my first ideas, and physical, especially hydrodynamical, demonstrations of the theorems I am now about to write out for my paper on "Magnetism" for the Royal Society, from rough drafts written in August 1848. W. T., October 29, 1849.\* The 'now' has been deferred until the present time, November 20, 1871. I am obliged to write from memory, as I have not been able to recover any of those rough drafts . . . ." The chapter consists largely of theorems of existence and determinacy of magnetic distributions, corresponding to assigned conditions over the boundary of the region, which are established and enforced from the analogy of liquid flux.

To the British Association at Oxford, in 1867, he explained concisely† and on modern lines how all the phenomena of terrestrial magnetism could be represented as the effect of a calculable ideal sheet of electric current spread over the surface, whether spherical or otherwise.

The continuation of the memoir on Magnetism of 1849–50, which treated of the "Theory of Magnetic Induction in Crystalline and Non-crystalline Substances," overflowed into another Journal‡ in 1851. He begins by recounting how Poisson in his third memoir on Magnetism (1823) had already contemplated the effect of crystalline arrangement of the 'magnetic elements' within which the neutral 'magnetic fluid' was considered to be separable by the field so as to produce polarity: non-sphericity of form (or any æolotropy) would also be potent, for the axes of the elements would all be similarly orientated. The subject was dropped by Poisson, after arriving at the linear vector form of relation, of unrestricted type, however, connecting the induced magnetisation and the magnetising force: he remarks that it would be curious to test whether crystallised substances actually exhibited such directional effects. Thomson points out that "a recent discovery of Plücker's had established the very circumstance," which now makes obvious the importance of working out a mathematical theory. As in the earlier memoir, a main object is to replace the artificial conception of a magnetic fluid by distribution of magnetic polarity, which is all that is objectively ascertainable, combined with the hypothesis of simple superposition of effects—restricted, however, to feebly magnetic material, to ensure

\* 'Elec. and Mag.,' p. 458.

† 'Elec. and Mag.,' pp. 468–70.

‡ 'Phil. Mag.,' March 1851; 'Elec. and Mag.,' pp. 471–87.

that the equations of magnetisation are thus linear. Then he considers the magnetisation of a small crystalline sphere situated in a uniform field. He asserts the existence of three principal magnetic axes in the crystal, which he is tempted in a footnote to identify with the known principal axes of optical elasticity. He expresses the torque acting on such a sphere, by aid of the hypothesis of superposition of magnetisations due to the components of the inducing field along these principal magnetic axes. Then he gets to the expression of a work-function depending on position and orientation, in the various spacial gradients of which the translational forcive is involved as well as this rotational forcive.

As he now remarks, he had recently obtained\* this work-function for the simpler case of isotropic material in the form  $\frac{1}{2}\kappa H^2 \delta \text{vol.}$ , and established by means of it the theoretical validity of Faraday's principle derived from observation, the tendency of magnetisable matter to travel towards regions of more intense force. He now extends it to the general case. He inquires of Faraday whether he had noticed that a piece of bismuth was repelled differently according to its orientation, a question already suggested by Poisson at the very beginnings of the subject. Then he cites Faraday's suggestion of two years before (December 1848), assigning inductive quality, varying with direction, as the cause of the definite orientation of a small crystalline mass near a powerful magnetic pole, which shows that Faraday had propounded the same question for himself. The question was immediately answered, in the manner anticipated, in experiments of Tyndall. Then he throws out a suggestion of the curious results obtainable with a crystal, immersed in fluid of inductive power intermediate between its own greatest and least crystalline inductive powers.

An appendix to this paper makes the quotations from Poisson's memoir referred to above. Then it proceeds to a remark which illuminates the whole subject. After reporting Poisson's general linear vector relation between magnetisation and force, involving nine coefficients reducible to one for isotropic matter, he proceeds as follows:—"and there is nothing to indicate the possibility of establishing any relations among the nine coefficients which must hold for matter in general. I have found that the following relations, reducing the number of independent coefficients from nine to six, must be fulfilled, whatever be the nature of the substance [namely, equality of the conjugate diagonal coefficients]; the demonstration being founded on no uncertain or special hypothesis, but on the principle that a sphere of matter of any kind, placed in a uniform field of force, and made to turn round an axis fixed perpendicular to the lines of force, cannot be an inexhaustible source of mechanical effect. All the conclusions with reference to magnecrystallic action enunciated in the preceding abstract are founded on these relations."

There the subject breaks off in 1851: something else had obtained posses-

\* 'Phil. Mag.,' October 1850; but see next page, referring to *Cambridge and Dublin Math. Journal*, 1847.

sion of the author's mind. Demonstration and elucidation are provided in the Reprint in 1872. The result was, perhaps, one of the most exquisite and brilliant mathematical applications\* of the principle of the Conservation of Energy that had yet or ever been made: not only did it show that every crystal must have three principal axes of magnetic induction, without any rotational quality, but the argument is also directly applicable to electrostatic induction, and is thus the essential feature in the immediate deduction by Maxwell thirteen years later of Fresnel's laws of optical double refraction from electric principles.

It may be recalled again in connexion with the above that Faraday's doctrine of flux in tubes of force and "conducting power for lines of force" dates from October 1850, and thus comes between Thomson's two memoirs described above.

It should also be recorded that the explanation of Faraday's principle, that a small soft iron sphere is urged towards regions of stronger force, belongs to a date as early as 1847.† But then the force urging the sphere is proved to be the gradient of the as yet uninterpreted function  $\frac{1}{2}\kappa H^2$  vol., obtained by direct calculation from the magnetic principles of Poisson; the remark that it was not until the autumn of 1847 that he had learnt the doctrine of Conservation of Energy from Joule has been quoted already. Helmholtz's 'Erhaltung der Kraft' appeared in July 1847.

Yet he triumphantly utilises this force-function to vindicate Faraday's profound view that a thin bar of diamagnetic material should point equatorially when placed in the line between magnetic poles. In a uniform field it *must* point axially, though with a force extremely feeble; but, quoting the words of Faraday,‡ "the cause of the pointing of the bar, of any oblong arrangement of the heavy glass, is now evident. It is merely a result of the tendency of the particles to move outwards, or into the positions of weakest magnetic action. The joint exertion of the action of all the particles brings it into the position which by experiment is found to belong to it." This doctrine proved difficult, and, in fact, became controversial, to some physicists unduly dominated by the simpler phenomena of forces of orientation, even Plücker's previous conclusions not being unexceptionable; and a good deal of attention was paid by Thomson at this time to its further elucidation and to very fascinating experimental illustrations. It is in a sense, possibly already in Faraday's own view, the generalisation of the hydrostatic principle of Archimedes, which would assert that in a field of power a more susceptible body will displace one less susceptible. The subject need not here be followed further.

Thomson and Maxwell both revert again and again to this crowning instance of Faraday's mathematical sagacity. Thus, to Thomson, in 1870,§

\* 'Elec. and Mag.,' p. 485.

† 'Cambridge and Dublin Math. Journal,' vol. 2, dated from Peterhouse, May 13.

‡ 'Exp. Res.,' No. 2269.

§ 'Elec. and Mag.,' p. 580.

"One of the most brilliant steps made in philosophical exposition of which any instance existed in the history of science, was that in which Faraday stated, in three or four words, intensely full of meaning, the law of the magnetic attraction and repulsion experienced by inductively magnetised bodies." And again, "Mathematicians were content to investigate . . . ; but Faraday, without mathematics, divined the result of the mathematical investigation ; and, what has proved of infinite value to the mathematicians themselves, he has given them an articulate language in which to express their results. . . . It must be said for the mathematicians that they greedily accepted it, and have ever since been most zealous in using it to the best advantage."

Incidentally it is of interest to note that Thomson's 'theoretical' physical solution of the problem of 'Mahomet's coffin,' to suspend a body in stable equilibrium in mid-space without supports or contacts of any kind, appears in this paper, the example being a diamagnetic sphere situated on the axial line of a straight vertical electromagnet.

If one had to specify a single department of activity to justify Lord Kelvin's fame, it would probably be his work in connexion with the establishment of the science of Energy, in the widest sense in which it is the most far-reaching construction of the last century in physical science. This doctrine has not only furnished a standard of industrial values which has enabled mechanical power in all its ramifications, however recondite its sources may be, to be measured with scientific precision as a commercial asset ; it has also, in its other aspect of the continual dissipation of available energy, created the doctrine of inorganic evolution and changed our conceptions of the material universe. A sketch of the early history of this doctrine will illustrate the innate power and independence of Lord Kelvin's thought, as well as in some degree his relations to his great predecessors and contemporaries.

The initial difficulty of the subject lay in the feature, entirely novel to physical science, that in the inorganic world what we call dissipation or scattering of energy is loss only in a subjective sense ; it concerns only the energy "available to man, for the production of mechanical effect," to use Thomson's own phrase of 1852.\* We can produce organised mechanical effect from diffuse energy such as heat, which consists in the unregulated motion of a crowd of jostling molecules, only by judicious guiding of its innate effort towards an equilibrium, just as we can get power from a turbulent waterfall by guiding the stream against a mill-wheel or turbine. But when the average of the molecular motions has come to a steady equilibrium throughout all parts of the material system, of which uniformity of temperature is the criterion, all chance of arranging or guiding part of its molecular energy into co-ordinated power available for our operations on finite bodies has passed away. This is, roughly, the *rationale* of the principle of Carnot. Yet the energy has not disappeared ; it is still there, but it is uniformly

\* 'Math. and Phys. Papers,' vol. 1, p. 505.

diffused and so not recoverable into the organised form of mechanical power. This absolute conservation of the total energy is the principle of Joule, which is the main experimental support of the presumption that all energy is ultimately of the dynamical type. In a complete view of physical transformations the two principles, of Carnot and of Joule, have both to find their places. Here a fundamental perplexity confronted and detained Lord Kelvin for some three years, 1847-50.\* When heat is allowed to flow away to a lower temperature without passing through an engine, its capacity for doing work has been dissipated. The opportunity for obtaining mechanical power from it has vanished beyond recall. Can then heat be correctly measurable as mechanical energy if some of the mechanical energy is lost irrecoverably every time that the heat diffuses to a lower temperature? Thomson, ever attracted by the engineering side of things, was dominated by Carnot's principle, as we have seen, even when as a youth, in 1845, he went to Paris to Regnault's laboratory. Thus he at once set himself to explore its practical content by the aid of the mass of exact data on gases acquired by Regnault, as soon as these results appeared, in 1847, as the first instalment of the famous series of experimental researches, which had been subsidised by the French Government with a view to obtaining all the data that could be pertinent towards the improvement of knowledge of the principles of steam and gas engines. In Thomson's first paper† towards this end, entitled "On an Absolute Thermometric Scale founded on Carnot's Theory of the Motive Power of Heat, and calculated from Regnault's Observations," he clears the ground for exact physical reasoning by elevating the idea of temperature from a mere featureless record of comparison of thermometers into a general principle of physical nature, making it a measure of the dynamical potentiality of heat, which is, on Carnot's principles, an intrinsic measure, *i.e.*, quite independent of the substances in which the heat happens to be contained. But he cannot get rid of the impression that heat is something different from energy, which may produce energy in falling to a lower level of temperature, or on the other hand may diffuse passively, so that this opportunity of creating energy is irrecoverably wasted. Such a view would tend towards the caloric theory which held that heat is somehow substantial; in terms of it Carnot, in fact, formulated his argument. It has been remarked on this by Helmholtz that if Carnot had then possessed completer knowledge he would possibly never have hit upon his principle; on the other hand, his rough

\* Cf. Osborne Reynolds' very illuminating "Life of Joule," forming vol. 6, 1892, of 'Mem. Manchester Lit. and Phil. Soc.' After the present notice had been prepared, the writer found that the early history of thermodynamics had been gone over by Professor E. Mach, of Vienna, in 'Die Principien der Wärmelehre historisch-kritisch entwickelt,' 1896, with results, in its restricted range of applications purely thermal, which seem to agree substantially with the views here taken. The development of the ideas and formulæ of the general science of energetics (*infra*, p. xlvii) by Thomson is thus not considered; while in most other special treatises it is almost entirely obscured by departure from the historical order of exposition.

† 'Proc. Cambridge Phil. Soc.,' June 1848.

manuscripts, published many years after, have revealed that during the remaining six years of his short life he was inclining strongly towards the correct view on the nature of heat. In a footnote, Thomson gives expression to his own doubt. The experiments of "Mr. Joule, of Manchester," seem "to indicate an actual conversion of mechanical effect into caloric. No experiment, however, is adduced in which the converse operation is exhibited; but it must be confessed that as yet much is involved in mystery with reference to these fundamental questions of Natural Philosophy." And in a fuller account, soon after, of Carnot's Theory,\* as further developed numerically by aid of the data given by Regnault's experiments on steam, he adheres substantially to this position, "although this, and with it every other branch of the Theory of Heat, may ultimately require to be reconstructed upon another foundation when our experimental data are more complete." He returns, in a note, stimulated by a remark of Joule, to the problem of what becomes of the mechanical effect that appears to be lost when heat diffuses; but he cannot admit the suggestion of Joule to cut the knot by abandoning Carnot's principle, and he appeals to further experiment "either for a verification of Carnot's axiom, and an explanation of the difficulty we have been considering: or for an entirely new basis for the Theory of Heat." Still harassed by these doubts, he returns yet again to test the experimental verification of Carnot's principle (which he finds adequate) in an Appendix;† for, as he says, "Nothing in the whole range of Natural Philosophy is more remarkable than the establishment of general laws by such a process of reasoning" as is that principle in its wider ramifications.

We have here found Thomson actually hesitating as to whether heat is to be classified as energy, on the ground that the fall of heat to a lower temperature can occur without developing any mechanical work. Yet it is true, as Lord Rayleigh has expressed it,‡ that most great authorities, especially in England, including Newton, Cavendish, Rumford, Young, Davy, etc., have always been in favour of the doctrine that heat is a mode of motion. The fact is, as we have seen, that Thomson knew too much to allow him to rest in such a partial view of things; he saw, also, a totally different side of the subject, which not even his close connexion with Joule, and appreciation of his work, could allow him merely to ignore.

Just a year before Thomson's first paper on Carnot's principle, Helmholtz, then a young army surgeon, had stepped (1847) into the first rank of physicists (though recognition came later, the memoir, *e.g.*, becoming known to Thomson only in 1852) by the publication of the 'Erhaltung der Kraft,' which asserted the universality of the conservation of total energy, and developed with convincing terseness and lucidity the ramifications of that principle throughout nature. To establish the transformation of heat into work he is already able to appeal to the classical experiments of Joule,

\* 'Trans. R. S. Edinburgh,' January 2, 1849.

† April 30, 1849.

‡ "The Scientific Work of Tyndall," 'Roy. Inst. Proc.,' March 16, 1894.

published three years previously (1844)—not yet mentioned by Thomson, whether it was from want of knowledge or from some fancied mode of evading their force in the light of his insistence on Carnot's principle. These experiments proved definitely that expansion of a gas working against the pressure of the atmosphere absorbs an equivalent of heat, whereas expansion into a vacuum absorbs none. It was, in fact, in this paper that Joule rather summarily condemned Carnot's principle as above mentioned, on account of its supposed discrepancy with his own established results. And Helmholtz had naturally to consider this point. He seems to have had access then only to Clapeyron's account of Carnot, of date 1843, from which, however, he expounds the argument succinctly and correctly. He admits the probability of the truth of Clapeyron's deductions for gases, but falls back on the suggestion that they may also be obtainable otherwise on more certain principles; while he characterises as very unlikely the (correct) inference that compression of water between its point of maximum density and the freezing-point would absorb heat. Thus Helmholtz,\* contrary to Thomson, saves the conservation of total energy by abandoning and ignoring the ideas belonging to the principle of Carnot.

The brilliant and suggestive writings of J. R. Mayer on the conservation of total energy were at that time unknown to Helmholtz: they seem to have been first brought to general notice† by Joule himself in the classical memoir on the Mechanical Equivalent of Heat presented by Faraday to the Royal Society in 1849. The sketch above given will have shown how little such theoretical considerations as those of Mayer, however illuminating and acute within their own range, were calculated to remove the profounder perplexities of Thomson, so long as there remained the apparently essential contradiction on which these doubts had their foundation. His insistence in class lectures on the absolute necessity for Joule's experimental work is still recalled by his students.

The credit of being the first to resolve these difficulties belongs to Clausius. In his memoir "On the Motive Power of Heat and the Laws of Heat which may be deduced therefrom," communicated to the Berlin Academy in February 1850, he quotes the title of Carnot's tract (Paris, 1824) in a footnote at the beginning‡ of the paper, which proceeds as follows:—"I have not been able to procure a copy of this work: I know it solely through the writings of Clapeyron and Thomson, from which latter are taken the passages hereafter cited." Then, in the introductory section, after referring to the difficulties above discussed, and the work of Holtzmann, Mayer, and Joule, he continues:—

"The difference between the two ways of regarding the subject has been seized with much greater clearness by W. Thomson, who has applied the recent investigations of Regnault, on the tension and latent heat of steam, to

\* 'Wissenschaftliche Abhandlungen,' vol. 1, p. 38.

† Osborne Reynolds, *loc. cit.*, p. 133.

‡ The quotations are from Hirst's translation, in which this memoir occupies pp. 14-68.

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From a Daguerotype

*Yours always truly  
William Thomas*

1854





the completing of the memoir of Carnot.\* Thomson mentions distinctly the obstacles which lie in the way of an unconditional acceptance of Carnot's theory, referring particularly to the investigations of Joule, and dwelling on one principal objection to which the theory is liable. If it be even granted that the production of work, where the body in action remains in the same state after the production as before, is in all cases accompanied by a transmission of heat from a warm body to a cold one, it does not follow that by every such transmission work is produced, for the heat may be carried over by simple conduction; and in all such cases, if the transmission alone were the true equivalent of the work performed, an absolute loss of mechanical force must take place in nature, which is hardly conceivable. Notwithstanding this, however, he arrives at the conclusion that in the present state of science the principle assumed by Carnot is the most probable foundation for an investigation on the moving force of heat. He says: 'If we forsake this principle, we stumble immediately on innumerable other difficulties, which, without further experimental investigations, and an entirely new erection of the theory of heat, are altogether insurmountable.'

"I believe, nevertheless, that we ought not to suffer ourselves to be daunted by these difficulties; but that, on the contrary, we must look steadfastly into this theory which calls heat a motion, as in this way alone can we arrive at the means of establishing it or refuting it. Besides this, I do not imagine that the difficulties are so great as Thomson considers them to be; for although a certain alteration in our way of regarding the subject is necessary, still I find that this is in no case contradicted by *proved facts*. It is not even requisite to cast the theory of Carnot overboard; a thing difficult to be resolved upon, inasmuch as experience to a certain extent has shown a surprising coincidence therewith. On a nearer view of the case, we find that the new theory is opposed, not to the real fundamental principle of Carnot but to the addition 'no heat is lost'; for it is quite possible that in the production of work both may take place at the same time; a certain portion of heat may be consumed, and a further portion transmitted from a warm body to a cold one; and both portions may stand in a certain definite relation to the quantity of work produced. This will be made plainer as we proceed; and it will be moreover shown that the inferences to be drawn from both assumptions may not only exist together, but that they mutually support each other."

This memoir, as Willard Gibbs justly claims in his obituary notice (1889) of Clausius, laid securely the foundations of modern thermodynamics. But it seems equally true that this high merit lies mainly in the single remark at the end of the passage just quoted, which resolved the difficulties that had stopped Thomson; after that the development, though luminously accomplished, would have been plain sailing to any first-class intellect. Thomson's great memoir "On the Dynamical Theory of Heat,"† in which he at once

\* 'Trans. R. S. Edinburgh,' vol. 16.

† 'Trans. R. S. Edinburgh,' March 1851.

connects Clausius' name with that of Carnot, appeared the following year. After giving a demonstration of the principle of "Carnot and Clausius" (§ 13), he proceeds (§ 14) to say that, about a year before, he had adopted this principle in connexion with Joule's principle, notwithstanding that he could not then resolve the apparent discrepancy, as the basis of a practical investigation of the motive power of heat in air and steam engines. "It was not until the commencement of the present year that I found the demonstration given above . . . . It is with no wish to claim priority that I make these statements, as the merit of first establishing the proposition upon correct principles is entirely due to Clausius, who published his demonstration of it in the month of May last year, in the second part of his paper on the motive power of heat. I may be allowed to add that I have given the demonstration exactly as it occurred to me before I knew that Clausius had either enunciated or demonstrated the proposition . . . . The reasoning in each demonstration is strictly analogous to that which Carnot originally gave."

Once Thomson gets thus under weigh, as we have seen, by his own unaided efforts though anticipated by Clausius, he developes rapidly the thermal aspects of the subject, concurrently with Clausius and Rankine, but with wider generality, in particular avoiding their hypotheses connected with perfect gases. So little was he prepared to trust to a permanent gas thermometer as giving practically the intrinsic dynamical scale of temperature, that the following year he had already begun with Joule their series of laborious joint experiments to determine exactly how much the gas thermometers differ from the absolute scale. Their procedure was to deduce the result sought from observation of the slight cooling or heating produced by driving the gas under high pressure through a porous partition; with a perfect gas the process would be isothermal. When we consider that the results were to lead straight into the very core of molecular dynamics, the investigation may well rank to this day as one of the most striking advances in the record of physical science. It is noteworthy that Thomson in his own work kept on with the symbol for the unknown Carnot's function, until the dynamical scale had thus been experimentally investigated; though a gas thermometer was doubtless adequate to give to Clausius and Rankine indications of absolute temperature, so far as required for their preliminary approximate investigations over limited range. We have only to think of the modern physical undertakings steadily pushed downward toward the absolute zero of temperature, to realise that, except on the basis of Thomson's dynamical scale of 1847 and his method conjointly with Joule of exactly realising it in 1852, there could be no such thing as temperature in a scientific sense, and low temperature research would be devoid of most of its significance. These essential foundations for the scientific treatment of Energy were laid firmly in 1852, in a way that has held good without substantial modification ever since.

Perhaps this point, the rigorous scientific generality of the foundations on which he built from the beginning, could not be enforced more strongly than

by recalling that it is just this Thomson-Joule intrinsic cooling effect of expansion without external work, very slight under ordinary conditions, due merely to mutual separation of the molecules of the gas, that is the essential feature in the modern continuous processes for liquefaction of even the most refractory gases, by the expenditure of mechanical power to abstract the heat, which have now become familiar. On the other hand, the great economy of the reversed Carnot gas-cycle for ordinary refrigeration was pointed out in 1852, and applied by his brother to the ventilation of Belfast College.

In their parallel developments of the subject, while Clausius kept mainly to the theory of heat engines, applications over the whole domain of physical science crowded on Thomson. Already in December 1851, he communicates to the Royal Society of Edinburgh his Theory of Thermo-electric Phenomena, including the classical prediction of the convection of heat by the electric current, the so-called Thomson effect, which in the theory of electrons has a literal title to its original name. The formulæ of the printed abstract\* of this paper show that he must have been already in full command (December 1851) of Carnot's principle in its most generalised form,—viz., as he expressed it in May 1854, but there introducing absolute temperature  $T$ , then recently determined by himself and Joule,—that in a complete reversible cycle of change  $\Sigma(H/T)$  vanishes, or in differential notation  $\int(dH/T) = 0$ , a form which was independently given by Clausius in December 1854, and from which the transition to Clausius' entropy-function (1856) is but a step. These advances appeared in full in the memoir, 'Trans. R. S. Edin.,' 1854,† where, in the way customary with him, he passes on to a long digression on the thermo-electrics of crystalline matter, including, after Stokes, the full theory of rotational vector effects. This latter subject was brought again into prominence many years after, when times were riper for it, with reference back to the present exposition, on the announcement by E. H. Hall of the discovery of an influence of this kind in electric conduction in a powerful magnetic field. Here also shines forth in a notable example what was always a main feature of Thomson's theoretical activity, the utilisation to the utmost of models and images of physical phenomena. He absolutely refused to deny to matter, however continuous and uniform as to sense it might appear to be, the possession of any property which he could imitate in a lattice structure or other architectural model, however complex; clearly, in his view, one has no right to assign limits *a priori* to the possible physical complexity of molecular aggregation.

One type of such limits, indeed, the only ones *a priori*, he vindicated in one of his most refined theoretical advances, those, namely, which are imposed on reversible phenomena by the principle of the conservation of energy. The demonstration on these lines that there can be no rotational quality in either magnetic or dielectric excitation in continuous media afterwards became, in Maxwell's hands, one of the main confirmations in the general

\* 'Math. and Phys. Papers,' vol. 1, pp. 316–323.

† *Loc. cit.*, pp. 232–261.

electric interpretation of optics, by leading at once to the validity of Fresnel's theory of double refraction. *Cf. supra*, p. xxviii.

But we must return from this digression. The cosmical aspect of Carnot's principle, in its reconciliation with that of Joule, had immediately arrested Thomson's attention, and the fundamental law of Dissipation of Energy in natural phenomena stood revealed in a brief note in April 1852, embodying the following momentous and carefully formulated conclusions\* :—

"1. There is at present in the material world a universal tendency to the dissipation of mechanical energy.

"2. Any *restoration* of mechanical energy, without more than an equivalent dissipation, is impossible in inanimate material processes, and is probably never effected by means of organised matter, either endowed with vegetable life or subject to the will of an animated creature.

"3. Within a finite period of time past, the Earth must have been, and within a finite period of time to come the Earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be, performed, which are impossible under the laws to which the known operations going on at present in the material world are subject."

It is of interest to contrast this principle of degradation, or diffusion, of energy towards a uniform equilibrium, with the other great principle, dominating the phenomena of the organic world, which took shape at about the same time. Just fifty years ago biological thought was startled with the idea of the gradual evolution of organic forms, by the persistence, through hereditary transmission, of such accidental modifications as are adapted to the surrounding conditions of life, to the existing environment. In inorganic phenomena the energy becomes distributed among merely passive molecules; in the organic world the unit of investigation is an organism which has apparently the active property of fixing and transmitting in its descendants any structural peculiarity that it may come by. But even here there is something in common; the automatic evolution towards improved adaptation, in this case with no limit or equilibrium yet in sight, is attained at the cost of compensating dissipation, namely, the destruction of the individuals that happen to be ill adapted even though in other respects superior.

We observe in passing that in Thomson's formulation, Clause 2 already implies Clausius' conception (1854) of compensating transformations. What is perhaps now more interesting is that it expresses a decided opinion (which he still retained in 1892) on a question which Helmholtz† to the end preferred to leave open, namely, whether the refinements of minute structure and adaptation in vital organisms may permit departure from the law of dissipation, which is known to be inflexible in the inorganic world, by utilising to some extent diffuse thermal energy for the production of vital mechanical power. The development of Clause 3 led to the famous series of investiga-

\* *Loc. cit.*, p. 514.

† See an interesting passage in his *Lectures on Heat*, posthumously published.

tions and discussions regarding the beginnings and the ultimate fate of our universe, and the duration of geological time, which have formed a region of intimate contact, but not always of agreement, between dynamical and evolutionary science.

Earlier in the same note, and also more fully in 'Phil. Mag.,' February 1853, Thomson illustrated his early complete grasp of all matters relating to the availability of thermal energy and to compensating transformations, in calculating the dissipation which arises from throttling steam, and the work which can theoretically be gained from the thermal energy in an unequally heated space.

This history is, however, not yet complete. Examination of the 'Notes inédites' of Sadi Carnot, appended to the reprint of the 'Réflexions,' published with charming biographical detail by his brother in 1878, and welcomed enthusiastically by Lord Kelvin, leaves an impression that Carnot was already struggling with difficulties of the kind to which the insight of Thomson exposed him some twenty years later. He had analysed (p. 91), with sure instinct, the Gay-Lussac experiment concerning heat of expansion of gas by efflux, and afterwards developed it (p. 96) into a suggestion of the identical porous plug experiment of Joule and Thomson. He points out (p. 92) that the view that heat is "le résultat d'un mouvement vibratoire des molécules" conforms to our knowledge in a long list of the principal transformations of energy; "mais il serait difficile de dire pourquoi, dans le développement de la puissance motrice par la chaleur, un corps froid est nécessaire, pourquoi, en consommant la chaleur d'un corps échauffé, on ne peut pas produire du mouvement." He seems to be trying (p. 94) to think out a definite distinction between this movement of the particles of bodies and the "puissance motrice" into which it cannot be changed back. "Si les molécules des corps ne sont jamais en contact intime les unes avec les autres, quelles que soient les forces qui les séparent ou les attirent, il ne peut jamais y avoir ni production, ni perte, de puissance motrice dans la nature. Alors le rétablissement d'équilibre immédiat du calorique et son rétablissement avec production de puissance motrice seraient essentiellement différents l'un et l'autre." "La chaleur n'est autre chose que la puissance motrice, ou plutôt que le mouvement qui a changé de forme. C'est un mouvement dans les particules des corps. Partout où il y a destruction de puissance motrice, il y a, en même temps, production de chaleur," and reciprocally. Like Thomson at the later date, he intended to seek the guidance of further experiment, outlines of which he sketched. These extracts suggest the very problems which are still fundamental in the molecular theory of energetics, about which much is yet to be learned, though Thomson's theory of dissipation of energy and its molecular interpretation by Maxwell and Thomson and Boltzmann has illuminated the whole field. Yet Carnot already saw (p. 93) that his negation of perpetual motion demands that when heat does work in falling to a lower temperature, if

some heat is really absorbed in the process the amount so absorbed must be independent of the mechanism of the process, must, in fact, be an equivalent of the work; for if the other alternative were possible, "on pourrait créer de la puissance motrice sans consommation de combustible et par simple destruction de la chaleur des corps." Clausius and Thomson had nothing in 1850 to add to this reasoning of date earlier than 1832.

No apology is required for thus dwelling at length on this episode in the evolution of the principles of physical science, the development of the principle of energy into its wider aspect, in which it assumes its universal co-ordinating rôle as the principle of available energy,—involving its complete available conservation only in the limited class of phenomena that satisfy the Carnot test of being reversible, and in other cases emphasising the partial dissipation into diffused unavailable molecular energy which is characteristic of the operations of physical nature. No passage in the history of modern physics can, perhaps, compare with it in interest. In the other outstanding advance of the last century, the unravelment of the function of the æther as the sole means of intercommunication between the molecules of matter so as to constitute a *cosmos*, as the seat of the activities of radiation and of electric and chemical change, the problem to be solved was of a different type. The questions have there been more precise; they have suggested, and their investigation has been directed by, definite adaptable trains of experiment. But the pioneers in the theory of available energy had to probe among the *arcana* of common experience, in a manner which takes us back to the beginnings of dynamical science and recalls the efforts of Archimedes and Galileo and Pascal in detecting controlling principles in the maze of everyday phenomena.

The original stimulus to all this wide grasp of the relations of inanimate nature had its origin in the progress of mechanical invention, in the successful construction and operation of thermal engines. Irrespective of the problem of their industrial improvement, the detection of the essential features of this mechanical value of heat would appeal strongly to an analytical mind like that of Carnot. But his compact informing principle, as its content was ultimately developed in Thomson's hands, far transcended the special thermal problem from which it started; it now dominates the whole range of physical science. It is only on its validity that our confidence is based, that we can treat the interactions of the finite bodies of our experience by strict mathematical and dynamical reasoning, entirely leaving aside, as self-balanced and inoperative, those erratic though statistically regular motions of the molecules, forming a very considerable part of the total energy, which constitute heat in equilibrium.

This fundamental basis of our knowledge of inanimate nature, thus acquired from clues suggested by human industrial improvements, still retains an aspect essentially anthropomorphic; it is conditioned by the limitations of our outlook as determined by the coarseness of our senses, as Maxwell seems

to have been the first definitely to perceive. For the case of an ultra-material sentient creature of bodily size so small as to be comparable with a single chemical atom, his own sensible physical universe would be controlled by some fundamental law possibly of quite different type, while the phenomena which are prominent to us would take on for him a cosmical character as regards both time and space. We can ourselves catch partial glimpses of such a transformed physical universe, not subject to ordinary laws of matter in bulk, in the phenomena of high vacua, where the gaseous molecules come nearly individually before our attention and can almost be counted, and in the recent cognate phenomena of radio-activity either spontaneous or electrically excited. The boundary of demarcation of this new world from the universe which is dominated by the principle of available energy is naturally ill-defined: its exploration sheds light on both, and is perhaps the most interesting of the present activities of theoretical and practical physics.

Here also Lord Kelvin has played a part. Already, in 1852, he had prefixed to one of his papers the title "On the Sources available to *Man* for the Production of Mechanical Effect," as if in anticipation of this anthropomorphic side of the subject, first broached apparently by Maxwell in 1871 at the end of his "Theory of Heat," where he points out that it is only man's inability to obstruct passively the individual molecules at will that prevents the whole of their energy from being available, and shows how sentient agents capable of doing this could reverse the otherwise irrevocable course of diffusion of the energy in a gaseous medium.

Perhaps Thomson's own most systematic pronouncement on the inner significance of these relations is a short paper in 'Proc. R. S. Edin.'\* of date February 1874. He points out that the changes contemplated in abstract dynamics are strictly reversible; while in actual physical phenomena the absence of reversibility is conspicuous, a fact which was already embedded in the principle of dissipation of energy in 1852. Now "the essence of Joule's discovery that heat is diffused energy is the subjection of physical phenomena to dynamical law." Yet if we could reverse all inanimate motion, inorganic nature would unwind again its previous evolution; "and if the materialistic hypothesis of life were true, living creatures could grow backwards with conscious knowledge of the future but no memory of the past, and would again become unborn. But the real phenomena of life infinitely transcend human science, and speculation regarding consequences of their ultimate reversal is utterly unprofitable. Far otherwise, however, is it in respect to the reversal of the motions of matter uninfluenced by life, a very elementary consideration of which leads to the full explanation of this theory of dissipation of energy."†

He goes on to explain in graphic terms how an army of Maxwell's

\* Also 'Nature,' vol. 9, 1874, pp. 421-424; 'Phil. Mag.,' March 1892, pp. 291-299.

† Cf. Helmholtz's review already quoted, 'Nature,' vol. 32, 1885, 'Wiss. Abhandlungen,' vol. 3, p. 594.



'demons'\* stationed along an interface across a column of gas could produce various kinds of physical effect at will, either (i) establish a difference of pressure at the two sides without alteration of temperature, or (ii) *vice versa*, while the dynamical possessions of the system as a whole, the *total* energy and momentum, remain absolutely unchanged.

Then he considers a volume of gas, having initially different temperatures in different parts, and allowed to pass towards the ultimate uniformity which constitutes equilibrium of temperature, by inter-diffusion of the molecules, each of them carrying its energy and momentum. After a certain time imagine the velocities of all the molecules to be exactly reversed, and the crowd will retrace their previous course, the diffusion being thus undone, ultimately attaining again the initial state, after which however diffusion towards uniformity will again supervene. How are we to reconcile this uncompensated restoration of energy with the universality of the principle of degradation? "The number of molecules being finite, it is clear that small finite deviations from absolute precision in the reversal we have supposed would not obviate the resulting dis-equalisation in the distribution of energy. But the greater the number of molecules the shorter will be the time during which the disequalising will continue; and it is only when we regard the number of molecules as practically infinite that we can regard spontaneous disequalisation as practically impossible." Then he proposes a problem of probability concerning a region of gas containing a finite number of molecules, viz., to determine the chance that say nine-tenths of them shall be in the upper half of their enclosure and only one-tenth in the lower half at any instant. This is solved (readily) by aid of the Theory of Probability in an appendix. It is shown that however great the number of molecules be, provided it is finite, a time must ultimately arrive when an excess in any assigned ratio, either of molecules or of energy, is in the upper half of the region. If a region contain  $2.10^{12}$  molecules of oxygen and  $8.10^{12}$  of nitrogen, the chance of their being entirely separated so that the oxygen is in a specified fifth part of the vessel is merely about one against ten raised to the power  $2,173,220.10^6$ . On the other hand, if there are  $n$  molecules of the one gas and  $n'$  of the other, the distribution in a partial region which is a fraction  $e$  of the total space is exactly in the average proportion, that of  $n$  to  $n'$ , without any molecule of either kind in excess in that part, only for a fraction  $\{2\pi e(1-e)n^{\frac{1}{2}}n'^{\frac{1}{2}}\}^{-1}$  of the time: for the case above specified this is the fraction  $(4021.10^9)^{-1}$  of the total time, that is, only one second in five million years.

The latter illustration may be pushed further by adapting from Lord Rayleigh;† the chance that an even division giving  $n$  molecules in each half of the region may not be departed from by an excess of more than  $r$  in one half, with an equal defect in the other half, is the value of the well-known

\* Maxwell's 'Theory of Heat,' 1871, at the end.

† "On James Bernoulli's Theorem in Probabilities," 'Phil. Mag.,' 1889; 'Scientific Papers,' vol. 4, p. 375.

function  $2\pi^{-\frac{1}{2}} \int_0^r e^{-\tau} d\tau$ , wherein  $\tau = r/n^{\frac{1}{2}}$  which is supposed to be not very large. Thus there is an excess on one side exceeding  $n^{\frac{1}{2}}$  molecules, during about one-sixth of the whole time; thus in 1 c.c. of gas at atmospheric pressure there is an excess of six thousand million molecules in one specified half of its volume, for one-sixth of the time, while in smaller volumes of gas the relative excess in a specified half rapidly becomes greater. In fact, as all depends only on  $\tau$ , the chances of a given percentage of departure from the mean diminish so as to be proportional to  $n^{-\frac{1}{2}}$  when  $n$  is increased.

The short paper which has been described at length relates to the chance of uneven distribution of the molecules in space. But questions regarding the nature of temperature, according to Maxwell's illuminating conception for a gas, are concerned with the law of distribution of the velocities in the crowd of molecules. It does not involve a long step from Thomson's investigation of probabilities of spacial distribution to reach a new outlook into the inner molecular meaning of thermodynamics, for which science is indebted, in the first instance, to Boltzmann (1877).\* The principle of Clausius that the trend of an isolated system is toward states for which the entropy continually increases may be put alongside the principle that the general trend of a system of molecules is through a succession of states whose intrinsic probability of occurrence—in the sense illustrated above—continually increases. The suggestion presents itself at once that this probability is in some way a measure of the entropy of the system, at any rate in systems of which we know enough to be able to calculate the probability. Boltzmann carried the calculation through, much on the lines above sketched from Thomson, for a mass of gas, arriving at the result that the entropy of any collocation is in fact proportional to the logarithm of the probability of its occurrence. This logarithm of the measure of probability satisfies the conditions characteristic of entropy: for instance, it is additive. But it probes deeper than formal thermodynamics can do: the latter is restricted to systems in which each infinitesimal element has a temperature, *i.e.*, has its own internal heat motions already averaged. The new interpretation of entropy is not subject to such restriction: it applies to systems whose elements of volume are in the inchoate condition existing before they have settled down to a temperature at all. In ordinary matter this settling down is nearly instantaneous; perhaps it is only in radiometer problems connected with rarefied gases that the state of matter in which it has not a temperature can concern us. But in the theory of the radiations pervading an adiabatic enclosure, the whole radiation does not settle down at all to a common temperature unless there is molecular matter present which can interchange it by the process of absorption and emission; in the absence of absorbing matter the energy corresponding to each wave-length retains its own temperature. Thus we can see how this wider probability-theory of entropy,

\* Cf. 'Vorlesungen über Gastheorie,' 1896, p. 42.

which was first extended to radiation by Planck, is calculated to throw additional light, not derivable from formal thermodynamics, on the averaged constitution of the natural radiation which is in equilibrium of emission and absorption with molecular matter.

This digression into the most modern molecular theory has perhaps led us too far. The very interesting subject of the thermodynamics of radiation is only about twenty years old. Resting as it does fundamentally on the link with mechanical energy which is afforded by Maxwell's working pressure of radiation, Lord Kelvin would never admit its validity. The reason seems to be that he was never able to satisfy himself about any mechanical model of the relation of the atom to the æther that would give a mechanism for this pressural interaction between them. There are those who hold that the physical idea of an electron is sufficiently precise to make the *rationale* of light-pressure logical and secure. But Lord Kelvin would not consider it until he could visualise the whole process—see it in operation, as he used to say—to effect which completely would possibly go deeper than we may ever hope to penetrate; and this inability cut him off from what some consider to be the most refined and beautiful special development of the science which he founded.

The question naturally arises whether the establishment of the mathematical function that is fundamental for the theory of mechanical energy is not a subtler matter than this mere estimation of chances: in other modes of its investigation a powerful array of the dynamical properties of the medium is introduced. What becomes of them in the present aspect? The answer is that the chance cannot be estimated aright until we know all the conditions, dynamical and other, to which the distribution of molecules is subjected. The dynamical relations find their place as conditions restricting the possibilities of random distribution. If through ignorance some of them are overlooked, the chances will be in error; each new condition that is discovered modifies to some extent the whole process, and thus amends our knowledge.

But this aspect of entropy is quite in keeping with the subjective character, so to speak, of available energy. Objectively, the dissipation of energy is merely the progress towards an equilibrium. As regards the purposes of man, whole regions of available energy may exist, of which he is ignorant, because he does not happen to have learned how to use them. The amount of energy available at a given temperature in a lump of carbon is possibly not yet exactly known: the process of turning it into heat before utilising it of course wastes most of it. Once, however, any slow reversible method of combustion has been discovered, in a voltaic battery for instance, the determination will be possible and may be effected once for all. Or, following a hint thrown out by Lord Rayleigh in 1875, afterwards developed more fully by Gibbs, we may make a rough estimate by applying the Carnot-Clausius formula to a cycle of which the upper temperature is that of spontaneous dissociation of the materials. We can, in fact, ascertain avail-

able energies only for systems which we can reach from a standard one by processes reversible in Carnot's sense.

Very early in Joule's investigations (1841) on the quantitative equivalence of various kinds of energy, he attacked the problem of the voltaic cell, and found his expectation verified, that in many cases the electromotive force was proportional to the thermal value of the chemical action of one Faraday equivalent of the reagent materials,—provided he employed\* “galvanic arrangements adapted to allow the combinations to take place without any evolution of heat in their own localities.” He concluded that the condition thus laid down must be departed from in certain observed cases of discrepancy, and Thomson, in 1852,† conducted experiments to detect such local reversible heat. This principle of Joule was also stated quantitatively later, in a general way, by Helmholtz in the ‘*Erhaltung der Kraft*’ in 1847. It lies at the foundation of Thomson's memoir of December 1851, “On the Mechanical Theory of Electrolysis,” whence the restriction above stated, the absence of local reversible heat, is quoted. *On this condition* the principle is exact; and the main point of Thomson's paper is the calculation, with a view to comparison with direct experiment, of the theoretical absolute value of the electromotive force of a Daniell's cell, from Joule's measurements of the heat developed by the combination of an electrochemical equivalent of its materials. The paper also developed the parallel between chemical energy and mechanical energy as sources of electromotive force, including the deduction by the principle of energy of the force induced by motion of a circuit across a permanent magnetic field. The further prosecution of the main subject, into cases where local reversible heat is developed (as evidenced by sensible change in electric conditions with temperature), remained for Gibbs and Helmholtz twenty-four years afterwards. In another paper of the same date, on absolute electric measurement, Thomson discusses Joule's thermal determination of absolute electric resistance of 1846, which afterwards proved to be more correct than the earlier values of the ohm.

Most interesting in connexion with modern ideas is an abstract of February 5, 1852,‡ again mainly expounding Joule's inspiring results and views on the transformations of energy. Thomson estimates from Liebig's data that about one-thousandth part of the total solar radiation incident on forest land is absorbed usefully by the trees, that being the amount recoverable as heat by their combustion. An intention to discuss these matters in connexion with Carnot's principle, dealing also with the wave-lengths of the radiation, does not appear to have been fulfilled. Passing on to animal work, he estimates, after Joule, that as much as one-sixth of the energy of the food consumed can go directly into mechanical power. Then, relying

\* ‘Math. and Phys. Papers,’ vol. i, p. 477.

† *Loc. cit.*, p. 503 : cf. also p. 496, where, in agreement with Joule, he ascribes the main loss to the work done by evolved gases in expanding against the atmospheric pressure.

‡ *Loc. cit.*, p. 505.

on Carnot's principle, and Joule's discoveries regarding the heat of electrolysis and of electromagnetism, he proceeds to argue that "it is nearly certain that when an animal works against resisting forces, there is not a *conversion of heat into external mechanical effect*, but the full thermal equivalent of the chemical force is *never produced*,—in other words, that the animal body does not act as a *thermodynamic engine*; and very probable that the chemical forces produce the external mechanical effects through electrical means."

Here he is emerging from the narrower theory of heat to the general theory of available energy, where heat is not the intermediary towards mechanical power; and we shall see presently how quickly he progressed in it. When it is recalled that at the time all this was going on, or immediately after, he was also laying the dynamical foundations of the phenomena of induced electric currents, including, for example, the calculation of the period of the vibrations produced by electric discharges, the activity may well seem unprecedented; adequate exposition of the results had to fall behind.

The next stage (1855) in this series of investigations, the development of the ideas expressed in the extract just quoted, seems to demand special attention, for it is surely nothing less than the laying down of the precise laws of the all-embracing modern science of free or Available Energy. The evolution of this generalisation can, as it happens, be traced. The memoir on "A Mathematical Theory of Magnetism" has been already alluded to. In it, as everywhere else in Thomson's dynamical writings, the conservation of the potential energy, used there in the manner of Lagrange and Green and MacCullagh and Helmholtz, in the sense of a potential of mechanical forces, is employed to determine the essential relations between physical properties. This use of the law of energy as a connecting principle afterwards became the note of Thomson and Tait's 'Treatise on Natural Philosophy.' In revising for press a continuation of this magnetic memoir, 'Phil. Mag.,' April 1855, where he is engaged in deducing magnetic reciprocal relations in more elementary fashion by use of a work-cycle, a thought occurred to him and was embodied in a footnote under date March 26, which will be quoted in full.\*

"It might be objected that perhaps the magnet, in the motion carried on as described, would absorb heat and convert it into mechanical effect, and therefore that there would be no absurdity in admitting the hypothesis of a continued development of energy. This objection, which has occurred to me since the present paper was written, is perfectly valid against the reason

\* 'Elec. and Mag.,' § 672. In a less definite way this principle had been effective long before, as the writer is reminded by Mach's historical account. Early in 1849 James Thomson explains that it was his brother's pointing out to him that, on Carnot's principle, water could be frozen isothermally without requiring mechanical work, which set him on to the train of thought that predicted the lowering of the freezing-point by pressure and calculated its amount. As freezing is accompanied by expansion, a cycle involving freezing at a high pressure and melting at a low pressure, in fact confronted him with a perpetual motion, which he had to evade.

assigned in the text for rejecting that hypothesis; but the second law of the dynamical theory of heat (the principle discovered by Carnot and introduced by Clausius and myself into the dynamical theory, of which, after Joule's law, it completes the foundation) shows the true reason for rejecting it, and establishes the validity of the remainder of the reasoning in the text. In fact the only absurdity that would be involved in admitting the hypothesis that there is either more or less work spent in one part of the motion than lost in the other, would be the supposition that a thermodynamic engine could absorb heat from matter in its neighbourhood, and either convert it wholly into mechanical effect, or convert a part into mechanical effect and emit the remainder into a body at a higher temperature than that from which the supply is drawn. The investigation of a new branch of thermo-dynamics, which I intend shortly to communicate to the Royal Society of Edinburgh, shows that the magnet (if of magnetised steel) does really experience a cooling effect when its pole is carried from  $A$  to  $B$ , and would experience a heating effect if carried in the reverse direction. But the same investigation also shows that the magnet must absorb just as much heat to keep up its temperature during the motion of its pole *with* the force, along  $AB$ , as it must emit to keep from rising in temperature when its pole is carried *against* the force, along  $DC$ ."

The exposition of the new branch of thermodynamics here referred to appeared (*cf. supra*, p. xiv) in the same month, April 1855, in the first part of the first volume of the 'Quarterly Journal of Mathematics,' under the title "On the Thermoelastic and Thermomagnetic Properties of Matter, Part I," which represents the contents of the latter part of the paper, to which the more general introductory matter was probably added. This paper was reprinted in 'Phil. Mag.,' January 1878, with some additional notes.\* The principles that we are now concerned with occupy the first few pages; the argument is expressed in terms of elastic strain, but that is obviously only for convenience of exposition. The total intrinsic energy  $\epsilon$  of a material system, measured from a standard initial configuration and temperature, is defined as a function of its actual configuration and temperature. It is established from Carnot's principle, as in the quotation above, that for transformations conducted entirely at the same definite temperature  $t$ , the mechanical forces applied to the system must be derivable from a work function  $w$  which represents, in fact, the potential energy acquired by the system in passing at that temperature from the standard configuration to the actual one. If  $\epsilon$  denote the simultaneous increment of  $\epsilon$ , then  $\epsilon - w$  must be the heat  $H$  taken in from outside during that change from the standard configuration, when conducted at the actual temperature.

It is to be observed that this simple consideration, which apparently here appears in science for the first time, carries the principle of potential energy in its mechanical application right back to Carnot's principle of 1824. In the

\* 'Math. and Phys. Papers,' vol. 1, pp. 291-316.

previous writings on general potential energy, such as Helmholtz's 'Erhaltung der Kraft,' nothing of the kind is hinted at; while Clausius' treatment, being restricted to transformation of heat, is nowhere connected up with the general theory of energy. The first law of Thermodynamics henceforth drops to more restricted scope, for it merely asserts that available energy when lost is changed into heat in equivalent amount. Yet it still suffices to maintain the presumption that all energy-processes have their source in—are consistent with—the ordinary Newtonian principles of dynamics as applied to ultimate molecules; considering the difficulty experienced by Thomson in reconciling Joule's law with his innate conviction of the validity of Carnot's principle, it is not surprising that this inference appealed to him with special force. Indeed, when the historical conflict between the two laws is kept in mind, the value of the first will not be disparaged. From this point of view the principle of Carnot appears in transformed aspect. Its chief interest is now transferred to the two creative ideas which it contains, the introduction into science (i) of the idea of a complete cycle of transformations, and (ii) of the criterion of absence of waste of power in any mechanical process, namely, that the process can be reversed, which includes the condition of temperature uniform throughout the system at each instant. The further development, including Carnot's function and the quantitative determination of the idea of temperature which it brings with it, is the thermal completion of these fundamental principles of the general science of Energetics. When the illustrious originator of these ideas died in 1832 at the age of 36 he was in possession of the material to complete the train of essential principles himself.

Thus far we have secured a work-function  $w$  (available energy) for the applied forces at each temperature  $t$ , of form determinable by direct experiment. If such a function were known for every temperature, knowledge of the mechanical energy relations of the system would be complete. Thomson accordingly proceeds to connect these functions for adjacent temperatures by means of a Carnot cycle. In fact, he shows how to construct  $w$  as a function of both the configuration and the temperature, so that the same function shall, for each constant temperature, represent the energy then available for work.

The cycle which he employs is quite general, irrespective of the type of configuration for which it is conducted. In fact, consider any definite change of configuration effected at temperature  $t$  and annulled at an infinitesimally near temperature  $t + \delta t$ , so that no work is done at the two infinitesimal transitions from the one temperature to the other, which complete the cycle. There will be heat  $H$  taken in at temperature  $t$ , and  $H + \delta H$  given out at temperature  $t + \delta t$ , while there will be heat  $\frac{\partial e}{\partial t} \delta t$  taken in at the upper transition, and  $\frac{\partial e_0}{\partial t} \delta t$  given out at the lower, each of the latter heats being at an average temperature  $t + \frac{1}{2}\delta t$ ; also if the lower configuration is taken to

be the standard one  $e - e_0 = \epsilon$ . Thus the equation  $\Sigma (H/t) = 0$  of Carnot-Clausius leads to

$$\frac{H}{t} - \frac{H + \delta H}{t + \delta t} + \frac{\partial \epsilon / \partial t \cdot \delta t}{t + \frac{1}{2} \delta t} = 0,$$

which is, in its exact limiting form,

$$\frac{\partial \epsilon}{\partial t} = t \frac{\partial}{\partial t} \frac{H}{t}. \quad (5^*)$$

Substitution from  $\epsilon = w + H$  gives the equivalent forms

$$\frac{H}{t} = - \frac{\partial w}{\partial t}, \quad (6)$$

$$\epsilon = w - t \frac{\partial w}{\partial t}; \quad (7)$$

so that, when the temperature changes as well as the configuration,

$$e = \int_{e_0}^t \kappa dt + w - t \frac{\partial w}{\partial t}, \quad (8)$$

where  $\kappa$  is the specific heat of the mass at  $t$  when maintained in the standard configuration. This latter equation determines the total energy  $e$  from the mechanical observations giving  $w$ , which is the work required to pass at temperature  $t$  from the standard configuration to the actual one.

Conversely, by (5), for a particular configuration,

$$H = t \int \frac{d\epsilon}{t}, \quad (10)$$

and, for a constant temperature,

$$w = \epsilon - H, \quad (11)$$

"which show how  $H$  and  $w$  may be determined for all temperatures from a knowledge of the intrinsic energy of the body, and of [one of] those functions themselves for a particular temperature."

The slight correction "[one of]" introduced in the Reprint (1882) is evidence of importance attached by Thomson to this investigation; yet it seems to have escaped general appreciation. On being asked about a year ago why he had been content with this brief, almost incidental, indication, and had never returned to the exposition of these fundamental quantitative relations of Available Energy, the letter in reply was simply to the effect "Yes; it is all there; there is nothing to be added."†

The two functions, total energy  $e$ , and work of available energy  $w$ , on

\* The equations are numbered as in Thomson's paper of 1855;  $H$  is here supposed expressed in units of energy, so that the factor  $J$  is omitted.

† In a brief note "On Thermodynamics founded on Motivity and Energy," 'Roy. Soc. Edin., Proc.' March 21, 1898, Lord Kelvin has himself recalled attention to the generality of this paper of 1855.



which the complete science of Energy is thus founded, are naturally to be compared with the two functions, energy  $U$  and entropy  $S$ , which were made fundamental by Clausius in the very same month, April 1855—the tendency of the entropy of a *self-contained system* to increase being his mode of exact expression by Thomson's principle of dissipation. In fact, the distinction between the two methods is that Thomson's function  $w$  refers primarily to a system fed with heat so as to remain at constant temperature, while Clausius' function  $S$  refers primarily to an isolated system.

The principal operations of chemistry and physics are performed at constant temperature; thus it is Thomson's function  $w$  that is fundamental in the modern science of Energy, having been reintroduced by Willard Gibbs as "the characteristic function at constant temperature," and by Helmholtz as "free energy." The entropy is simpler to describe, and also to work with, except when the operations are isothermal; on the other hand the "free energy" is a direct physical conception connecting up heat-energy in line with all other types of available physical energy, and thus transforming thermodynamics into the universal science of the relations of the statical transformations of Energy, namely, Energetics.

The function entropy seems to have been never employed in Lord Kelvin's investigations. As may be inferred from the above, it did not lie directly in his line of thought, which concerned itself with the physical entities energy and work. The idea of entropy is so directly suggested by his principle of dissipation, and the early mastery of the Carnot-Clausius equation  $\int (dH/T) = 0$  for a reversible cycle in its widest form, which is shown in his theory of thermo-electric phenomena, that it could hardly have been strange to him; conceivably he never directly formulated it, because he had, in fact, developed a more directly physical scheme.

It is customary, after Thomson's own example, to call the relation  $\int (dH/T) = 0$ , as above, the Carnot-Clausius equation. It would provide the necessary complement to this nomenclature if the equation (7), that is, in more usual notation, the equation of energy  $A$  available at constant temperature  $T$ ,

$$A = E + T \frac{\partial A}{\partial T},$$

which is now the fundamental principle in chemical physics through the far-reaching applications made by Gibbs, Helmholtz, Van't Hoff, Nernst, and other investigators, were known as the Thomson equation. His dominating position is indeed already widely, but not very definitely, recognized.

The question whether Thomson had prior knowledge of the entropy principle has been matter of some controversy between Clausius and Tait: on the view here taken it is relatively unimportant.

We may now recall in general terms the form of the principle developed into most varied applications by Willard Gibbs, with such power and invention as to constitute him the creator of a new science. The necessary increase of the entropy function  $S$  defines the trend of adiabatic transforma-

tion; the necessary decrease of the available energy function  $A$  defines the trend of isothermal transformation.

The two functions are immediately connected by noticing that the  $S$  in the given configuration exceeds  $S_0$ , that in the standard configuration at the same temperature  $T$ , by  $-\partial A/\partial T$ . We can render an isothermal transformation adiabatic by including in the system an infinite reservoir of heat at its own temperature, in the manner favoured by Planck: the change of total entropy is that of  $S-H/T$ , so that this function must always increase in an isothermal system. The reverse transition from adiabatic to isothermal would not be so direct. In fact, the entropy  $S$  is the convenient analytical function to employ when the temperature is different in different parts of the system, as is illustrated by the complexity of the calculation (already conducted in February 1853, in terms of Carnot's function  $\mu$ ) of the energy available for mechanical effect in such a system when self-contained,\* which is mainly of cosmical interest, and has probably drawn attention away from the principles of free energy, though the latter were again emphasised in Thomson and Tait's 'Natural Philosophy.'

This analysis of available energy by Thomson had not escaped the notice of Willard Gibbs (1876), though possibly only in its narrower connexion with elasticity.† "Such a method is evidently preferable with regard to the directness with which the results are obtained. The method of this paper shows more distinctly the rôle of *energy* and *entropy* in the theory of equilibrium, and can be extended more naturally to those dynamical problems in which motions take place under the condition of constancy of entropy of the elements of a solid . . . just as the other method can be more naturally extended to dynamical problems in which the temperature is constant." Gibbs then refers back to a previous note explaining the wider generality of his own method: its most salient feature is, however, the far wider development, by its author, into the doctrine of the chemical potentials of the constituent substances.

As throwing light on the stage at which scientific thought had arrived at the time Thomson was thus formulating the general science of Energetics, the following quotation from Helmholtz's important lecture,‡ "On the Interaction of Natural Forces,"—delivered first at Königsberg, February 7, 1854, and in which he was the first to refer the replenishment of Solar heat to gravitational shrinkage,—is pertinent to our history. "These consequences of the law of Carnot are, of course, only valid provided that the law when sufficiently tested proves to be universally correct. In the meantime there is little prospect of the law being proved incorrect. At all events we must admire the sagacity of Thomson, who, in the letters of a long-known little mathematical formula which only speaks of the heat, volume, and pressure

\* Thomson, *loc. cit.*, p. 554. The calculation of the final uniform temperature is in fact based (p. 556) implicitly on constancy of the entropy.

† 'Scientific Papers of J. Willard Gibbs,' vol. 1, p. 204.

‡ English translation (by Tyndall), vol. 1, 1873, p. 172.

of bodies, was able to discern consequences which threatened the universe, though certainly after an infinite period of time, with eternal death."

Later, in 1861, in writing of the constant surprises that arose in his work on acoustics, and the impression borne in upon him that new results develop themselves in the mind according to laws of their own, so that it seems to be hardly things essentially of his own invention that he is reporting, Helmholtz suggests that "Mr. Thomson must have found the same thing in his own work on the mechanical theory of heat."\*

At the meeting of the British Association at Belfast, in 1874, Andrews seems to have communicated verbally his results on the critical temperatures of mixed gases—only published posthumously in 1886—including the fact that the presence of nitrogen increases the quantity of carbonic acid that will evaporate into a given space. These results strongly attracted the attention of Maxwell, as appears in letters to Andrews of date 1874 and 1876,† the earlier referring to his own recent construction of Gibbs' thermodynamic surface; but it appears most remarkably in a letter to Stokes of date August 3, 1875,‡ in which he spelled out the whole abstract theory of the conditions of co-existence of two phases in a mixture of substances, exactly in the manner of Gibbs, and, moreover, looked forward to getting clearer ideas regarding the functions afterwards named by Gibbs the 'potentials' of the constituents, by applying the method to simple systems. At that very time Gibbs was preparing for press the profound and exhaustive treatment, over the entire range of known phenomena, and even into others yet unrecognised, which has become a classic in scientific literature.

One other important landmark in the development of Thermodynamics into Energetics is instructive historically. As Helmholtz afterwards discovered, the importance of the principle of dissipation of energy as the true criterion of chemical reaction was enforced by Lord Rayleigh in a discourse at the Royal Institution in 1875,§ in which, naturally without mathematical development, he pointed out the bearings of the criterion on the problem of solution of salt in water, on the modification by pressure of the equilibrium between carbonic acid gas and chalk, and in imposing a limit with rise of temperature to the combination of oxygen and hydrogen. In the first quantitative investigation of this kind, communicated to the 'Philosophical Magazine' in the same year, he calculates how much energy is dissipated by the isothermal mixture of two different gases, on the basis of a result of the kinetic theory. The conclusion, a very simple one, which immediately attracted the attention of both Maxwell and Gibbs, is, as he explains, verifiable at once by taking advantage of the reversible mode of separation afforded by absorbing one of the gases either by solution or by chemical action: it thus forms a stage towards the more daring introduction

\* 'Life,' p. 205.

† 'Scientific Papers of T. Andrews,' Introduction, p. liv.

‡ 'Memoir and Scientific Correspondence of Sir G. G. Stokes,' vol. 2, p. 34.

§ 'Scientific Papers,' vol. 1, p. 240.

by Gibbs of theoretical semi-permeable partitions of various kinds which has since become such a convenient and even practical feature in chemical physics.

Some confusion between the two main modes of development, that of entropy and that of available energy, to the detriment of the latter, was at one time accentuated by the misunderstanding\* of Clausius' function contained in the earlier editions of Maxwell's 'Theory of Heat,' but corrected in the fourth edition (1875), where, however, he is still far behind Thomson's definite position of 1855, for he sums up with the remark (p. 193) that "The calculation of the energy dissipated during any process is therefore much more difficult than that of the increase of the total entropy."

If, however, the researches into the principles of available energy are, from an abstract and philosophic point of view, the most striking of Lord Kelvin's achievements, the practical side of his genius operated more persistently in other ways, for example, in connexion with the introduction and establishment of a scientific system of measurement of electrical quantities. Not only did he enlarge and enforce the advantages of a universal correlated system of units, such as had been developed in the narrower field of the distribution of terrestrial gravity and terrestrial magnetism by Gauss and Weber because in fact they were indispensable to international co-operation in these subjects: he was also the prime mover in starting those determinations of absolute constants of nature and of numerical relations between the various natural standards, which, repeated and refined by a long line of eminent successors, are now the special care of governments, as affording the universal data on which modern exact engineering is ultimately based.

One of the main incitements to this development of electrical science on an exact basis of practical measurement was doubtless provided by the problem of submarine telegraphic communication. The earliest successful cable between this country and the Continent dates only from 1851; and the phenomena which obstructed its speed of working, both the amount of electricity which it took up, owing to its large capacity, before sensible effect could be produced at the other end, and the soakage into the insulating material, had come under the consideration of Faraday. These difficulties, as well as the mechanical obstacles to laying it, would be far greater in a longer cable; but already in 1857 the funds were forthcoming, owing mainly to the zeal of Cyrus Field, and a cable was laid to America. Thomson gave the project his strongest support, even becoming a director of the company responsible for the enterprise. But the methods adapted to signalling through so long a cable had not yet been developed: and mistaken attempts, on the part of those in charge of it, to accelerate the speed of working by feeding it with electricity of high tension, led soon to rupture of its insulation. Next year another cable was laid down and was operated

\* Pointed out by Gibbs in 1873, 'Scientific Papers,' vol. 1, p. 52, footnote.

successfully for a few weeks before it developed a fault. Thomson had now been given a free hand, and all his force must have been concentrated into carrying through to success the costly enterprise for which he had made himself responsible. He was now able to put into operation his own ideas: instead of strength or tension of current, he relied on the other alternative, extreme delicacy of the receiving instruments. At first he utilised, both in 1858 and on the later cables of 1865 and 1866, the galvanometer, adapted into its most sensitive form, by developing the method of Gauss and Weber of observing very slight motions of the very minute needle, situated at the centre of a small coil at first arranged on the Gaugain-Helmholtz plan, by the reflexion of a beam of light from it—using thus a non-material pointer, as he expressed it, whose length was not subject to limitation from any difficulties relating to weakness or weight or inertia. In 1870 he replaced this mode of reading signals from the oscillations of a spot of light, by a method which actually wrote the message on paper—the famous siphon recorder still employed for long cables. The magnet of his galvanometer had to be very small in order to get it into the cavity of the coil through which the cable-current flowed, so as to be in the most intense field of force relative to its size; and there was of course a limit to the magnetism it could retain. It was thus out of the question to attach to it directly the inertia of any writing apparatus. Thomson therefore reversed the circumstances: it was now the coil that was free to swing, and when the undulations of current passed through it, dead-beat oscillation ensued arising from its being suspended in the narrow concentrated field of a powerful magnet. In this *heterostatic* system of receiving signals or measuring effects, as he had called it in his early electrometers (1857),\* the mechanical force was capable of increase so long as the power of the accessory magnet could be increased: it was easy to get the magnet strong enough to permit the coil to carry a small siphon filled with ink, which spurted a permanent trace of its own transverse oscillations on an electrified sheet of paper moving lengthways beneath it.

It may be noted here that in delicate galvanometry, after a long reign of the original Thomson type of instrument with reflecting magnetic needle, the construction has largely passed over to this heterostatic form, first made convenient for ordinary work by d'Arsonval by the use of a permanent steel magnet. In the earlier days some direct measure of the relative magnitudes of currents was oftener needed: but the progress of electric standardising, and the consequent development of exact methods of balancing against such standards, have now made measuring arrangements so handy and convenient that variation of the scale due to gradual changes in the steel magnet is of little account.

It was perhaps the same necessities, the insulation of cables, that led him into exact investigation of the magnitude of the electric forces that would throw sparks across a given breadth of air or other material; though the

\* 'Elec. and Mag.,' pp. 262, 310.

development of the electrometers suitable for this purpose had begun with him very early in his career. His investigation of the attraction of two mutually influencing spheres had this object in view (*supra*, p. x); and he has put on record how, about the same time, 1846 or 1847, he was impressed by finding in the Cavendish manuscripts, then in the hands of Sir W. Snow Harris at Plymouth, his marvellous experimental determination of the capacity of a circular disc as compared with a sphere. An immediate application of the electrometer, as thus rendered absolute, was to the exact measurement of the voltaic effect of contact between different metals: it was found that connexion through a drop of electrolyte annulled the effect, and the meaning of this and related observations remained for long a matter of controversy, perhaps not yet settled. The continued improvement of standard electrometers, as distinct from mere electroscopes, was also stimulated by his interest in the problem of atmospheric electricity, in which he followed up the work of Beccaria. He was naturally an admirer of the science of the Earth's magnetism as it had been securely founded by Gauss and Weber: he seems to have conceived the aim, by the use of similar methods, namely, the steady collection and discussion of exact observations, of establishing a science of the Earth's electricity. The conditions were naturally far more complex: the wide and erratic fluctuations in an unstable meteorological phenomenon, such as the electricity of the atmosphere, were very intractable, in comparison with the more steady secular modes of change of the magnetic field of the Earth. Though even yet knowledge of the genesis of thunderstorms is very far from definite, the foundations of what is known are based largely on Thomson's pioneering investigations.

But no increase of mere instrumental sensitiveness could have availed to increase the speed of signalling in cables. The problem of how to obviate the deleterious diffusive effects due to electric capacity of the cable was one for mathematical study, on the methods of Thomson's own earliest mathematical writings, those of the Fourier Theory of Diffusion of Heat; for the electric impulse merely diffuses along such a cable, like heat along a bar, instead of being propagated by definite waves. Already in 1854 the outlines of the theory of the relation of length of cable to speed had been worked out in a correspondence,—apparently stimulated by Stokes, though he was always very generous in his acknowledgments,—which had only to be further developed in order to find the kind of compound electric impulses communicated at one end which would give quickest and most definite observable response at the other end. Throughout 1856 he insisted on the correctness of his principles, which were indeed mathematically irrefragable, in the 'Athenæum,' the 'Proceedings of the Royal Society,' and elsewhere, and as we have seen he was ultimately authorised to put them into practice.\*

At this time, too, he just touched on the other type of action, that of electrodynamic induction,† in the confusing of the propagation of signals, pointing out

\* Cf. 'Math. and Phys. Papers,' vol. 2, pp. 60—111.

† Cf. also 'Baltimore Lectures,' Appendix L.

that in ordinary telegraphy the alternations did not follow one another with rapidity sufficient to render this effect of practical importance. But with the invention of the telephone, transmitting the far more rapid vibrations of speech, it soon came to the front. Long afterwards (1889) in lecturing with keen appreciation on Heaviside's mathematical prescription, at first sight paradoxical, for removing the difficulties of long-distance telephony simply by interposing suitable inductance coils in the circuit, he recurs to some of his early experiences afloat with his associates the Atlantic cable engineers, recounting how they then knew from experience, and understood by reason, that even leakage was a good thing for cable signalling, provided they could have it where it was wanted without the risk of having too much of it.

Thus from about 1857 a main portion of Thomson's energies became diverted into other channels. The wonderful flow of new scientific principles, of permanent interest for all time, which was characteristic of the preceding twelve years, and is represented roughly by the first volume of his *Collected Papers*, is now largely suspended; his main activity is devoted to the (in some respects) more ephemeral, but equally valuable, aim of rendering available by mechanical appliances, for the purposes of practical life, the knowledge thus acquired. But when the troubles with the cables had been finally surmounted in 1867, by an experience which had made Thomson a resourceful engineer as well as a physicist, a new outburst of theoretical activity arrived.

Among the most potent causes of the general improvement in physical modes of thought during the last third of the century, was the appearance, in 1867, of what then purported to be merely the first volume of the '*Treatise on Natural Philosophy*' by W. Thomson and P. G. Tait, which has proved to be a turning point in the exposition and expression of physical science, at any rate in this country. The preparation of this book, which had gone on for some years, induced frequent visits by Thomson to his friend and disciple Tait at Edinburgh. Among other things, this treatise revised the terminology of dynamics, which had been allowed to grow up, in many respects, in forms that retained only historical meaning; the impulse thus given, which had indeed already been operating less systematically in the previous years, and was largely due doubtless to his brother James Thomson, has led in the hands of Maxwell, Heaviside, and others elsewhere, to greater attention to the language of science, the introduction everywhere of expressive terms, which react powerfully in inducing clearness of ideas. Another of the benefits conferred by this work was that it served, in some degree, to focus the scattered fragments of Thomson's own investigations and those of his associates, and to exhibit his scientific method, as exemplified in the subjects covered in this first instalment, which contained general kinematics and dynamics, general theory of the potential, and theory of elasticity with extensive geodetic application.

A translation of this book into German, by Helmholtz and Wertheim, appeared in 1871-4. In a preface, Helmholtz pointed out how it satisfied, in

very remarkable manner, a most urgent want in higher scientific literature. Previously there had been no resource but to go to original memoirs, difficult of access even if one knew where to find them; and on this account the recent progress of connected mathematical physical thought had been halting. Moreover, as he said, when a worker like Sir William Thomson admits us to participate in the very upbuilding of his ideas, exhibits to us the modes of intuition, the guiding threads, which have helped him, by bold combinations of thought, to control and arrange his refractory and entangled materials, the world owes him its highest gratitude. Helmholtz goes on to contrast the universal outlook of such a book, involving unavoidable lacunæ and difficult transitions, with the beautiful precision of the best special treatises of the earlier period. But the reader who does not spare himself the necessary effort towards mastery reaps an ample reward; he will find himself trained and equipped for the task of appreciating and extending knowledge, to a degree that he could never have attained from mere passive assimilation of sharply cut formal demonstrations. Valuable to the same end is the constant endeavour of such a work to employ those mathematical methods that keep close to actuality, are amenable to detailed interpretation; though they are usually much harder, especially at first, than a strictly ordered analytical calculus would be, there remains the permanent gain of direct insight into the processes and relations of nature. Finally, allusion is made to difficulties encountered by the translators, arising from the originality of the treatment, and the series of new scientific terms that the authors had, in consequence, introduced.

This appreciation, by the most competent living master, set out justly the advantages and defects of Thomson's method of work. He never had time to prepare complete formal memoirs. It was but rarely that his expositions were calculated to satisfy a reader whose interests were mainly logical; though they were almost always adapted to stimulate the scientific discontent and the further inquiry of students trained towards fresh outlook on the complex problem of reality, rather than to logical refinement and precision in knowledge already ascertained. Each step gained was thus a stimulus to further effort. This fluent character, and want of definite focus, has been a great obstacle to the appreciation of 'Thomson and Tait,' as it is still to Maxwell's 'Electricity,' for such readers as ask for demonstration, but find only suggestion and exploration. There is perhaps nothing that would contribute more at present to progress in physical thought than a reversion, partial at any rate, from the sharp limitation and rigour of some modern expositions to the healthy atmosphere of enticing vistas which usually pervades the work of the leaders in physical discovery. With increased attention to the inspired original sources of knowledge the functions of a teacher would be more than ever necessary, to point to the paths of progress and to contrast the effectiveness of different routes, as well as to restore valuable aspects which drop away in formal abstracts; science would thus adhere to the form of a body of improving doctrine rather than a collection of complete facts.



Readers of the 'Life of Helmholtz' will recognise how fruitful for knowledge was the intimate lifelong friendship between these two greatest investigators of the age. The 'Erhaltung der Kraft' of 1847 became known to Thomson about five years later, and he is insistent on the benefit conferred on British science by the appearance of a translation some years after in Taylor's 'Scientific Memoirs.' It was in August 1858, about the time Thomson's invention was perhaps at its highest development, that they first met. Thomson had written from Kreuznach urging Helmholtz to attend the British Association in September; he remarked that his presence would be one of the most interesting events of the meeting, and added the plea that he looked forward with the greatest pleasure to an opportunity for making his acquaintance such as he had desired ever since the 'Erhaltung der Kraft' had come into his hands. A few days later Helmholtz called on him, and reports as follows to his wife\* :—

"I expected to find the man, who is one of the first mathematical physicists in Europe, somewhat older than myself, and was not a little astonished when a very juvenile and exceedingly fair youth, who looked quite girlish, came forward. He had taken a room for me close by, and made me fetch my things from the hotel, and put up there. He is at Kreuznach for his wife's health. She appeared for a short time in the evening, and is a charming and intellectual lady, but in very bad health. He far exceeds all the great men of science with whom I have made personal acquaintance, in intelligence and lucidity and mobility of thought, so that I feel quite wooden beside him sometimes. As we did not get through nearly all we wanted to say yesterday, I hope you will let me stay over to-day at Kreuznach."

A record of the personal impression produced at this period, when he was not much known in London, on so close an observer of character as Thackeray, occurs in the recently published correspondence of the essayist Dr. John Brown of Edinburgh; it will supplement the above more scientific appreciation. Thackeray had been making one of the earliest of his lecturing tours, and had gone on from Glasgow to Edinburgh. Dr. Brown writes in humorous vein to Lord Kelvin's relative, Miss Crum, on November 11, 1856. "... He (Thackeray) was delighted with your William Thomson; he said he was an angel and better, and must have wings under his flannel waistcoat. I said he had, for I had seen them..." In later years Dr. Brown seems to have made a point of sending to his friend reports of Lord Kelvin's public appearances.

It is to be remembered that Helmholtz's early professorial work was physiology, which it continued to be until 1857, when as a by-product of his acoustical researches the memoir on Vortex Motion appeared, one of the most brilliant results of mathematical genius of all time. It seems to have been about ten years later that Thomson's attention was definitely arrested by this memoir; on watching Tait experiment on the rebound of

\* 'Life,' by Koenigsberger, Miss Welby's translation, p. 145.

smoke rings in air after collision, the theoretical illustration of material atoms which is afforded by vortex rings in a perfect fluid medium is said to have leaped into view. Great mathematical activity at once ensued. The fundamental memoir of Helmholtz reappeared translated by Tait in 1867, and Thomson's beautiful development of vortex theory, in which the principles, proved by the rigorous abstract analysis of Helmholtz, were worn down to the current coin of general ideas relating to circulation and vorticity and cyclic motions generally, appeared in 'Trans. R. S. Edin.' (pp. 217-260) in 1867-8. So great was the insight into the underlying world of individual molecules that Thomson thought might arise from the development of this vortex analogy, that at one period he is said to have grudged all the time that was not devoted to its study. His papers and miscellaneous notes on vortex motion have not yet been collected; they contain many *tours de force* and some of his very hardest thinking. Nowadays nobody imagines that the molecules of matter are merely vortex rings, and it is doubtful whether Thomson ever thought they were so in any strict literal sense; but his language was certainly calculated to leave that impression, and for years the fascination of that view prevailed. What is equally certain is that the vortex theory has been a beacon light in the *arcana* of the physics of molecules; such other illustrative theories as have been helpful in this direction have been its lineal descendants, so that points of view now stand out as legitimate and illuminating which before the days of the vortex theory could hardly have been conceived precisely at all.

At Easter, 1864, Helmholtz paid a visit to the Thomsons at Glasgow, with impressions again recorded in a letter to his wife.\* "I have seen a quantity of new and most ingenious apparatus and experiments, which have made the two days very interesting. He thinks so rapidly, however, that one has to get at the necessary information about the make of the instruments, etc., by a long string of questions, which he shies at. How his students understand him, without keeping him as strictly to the subject as I ventured to do, is a puzzle to me; still there were numbers of students in the laboratory, hard at work, and apparently quite understanding what they were about."

The recreation of yachting, by which Thomson was wont to recruit his energies in summer, reacted naturally towards the improvement of nautical affairs. His dynamical instinct, and experience in the invention of delicate instruments, found a congenial field in placing the ship's compass on a scientific basis. The heavy cumbersome magnets swinging on pivots under unsuitable conditions were replaced by the well-known systems of needles, delicately suspended yet insensitive to shock, so small that the iron masses compensating for the magnetism of the ship could be effectively introduced in moderate size. Again, by the use of steel wire he worked up the modern method of taking reliable soundings from a ship in motion, the depth being calculated from the compression of the air in a narrow glass tube attached to

\* 'Life,' *loc. cit.*, p. 233.

the sinker. But the most remarkable feat in this domain was the thorough practical mastery of the complicated phenomena of the tides, achieved mainly under his direction, and culminating in the invention about 1876 of simple automatic mechanism for performing all the laborious calculations of tidal harmonic analysis, both direct and inverse. The tides are controlled by the Sun and Moon, and so repeat themselves very closely in periods of nineteen years. But there is another far more fundamental and instructive way of investigating them. To every periodic (simple harmonic) component in the motion of either Sun or Moon relative to the Earth, there corresponds a component of the same periodic time in the tide produced by them at any place, and there are no other components; yet to calculate their amounts directly with the existing irregular contours and depths of the ocean would be a problem practically impossible. The method of harmonic analysis, as first initiated in this subject on a much smaller scale by Laplace, allows us to deduce, from a tidal record for a sufficient length of time, the amplitudes and phases of these harmonic components of known periods; and when the more important ones have been thus determined, the prediction of future tides becomes a matter of merely summing up the harmonic constituents, no matter how complex the physical conditions at the place in question may be, so long as they are unchanging. All this and much more can now be done by the machines invented by Lord Kelvin and his brother,\* though owing to the preliminary imperfection of construction of the analysing machine it is at present found to be safer and not very troublesome to determine the amplitudes of the components by calculation. This achievement—the complete mastery of the tides by means most simple but adequate—is perhaps the greatest triumph of the method of Fourier, which has always been one of the advances most admired by Lord Kelvin in modern physical mathematics. After this success it was natural to apply the same method of harmonic analysis to meteorological phenomena, including the atmospheric electricity which he had investigated many years before, which also are controlled by Solar influence; but here the problem has proved not to be so feasible, the definite periodic components being so mixed up with the erratic results of meteorological instabilities that not much has yet come out of the effort.

In later years Helmholtz paid many holiday visits at Largs and enjoyed the yachting expeditions, which provided a refuge for him from the attacks of hay fever. In 1871 the two friends studied the theory of waves which Thomson “loved to treat as a kind of race between us.” It was shortly before that Thomson had broken new ground suggested by observations from his becalmed yacht, on the theory of capillary ripples, and on the waves produced by wind and current, treated in two letters to Tait intended for the Royal Society of Edinburgh. In later years the latter subject was discussed in much more detail and developed in new directions by Helmholtz, with a view to meteorological atmospheric applications.†

\* See Thomson and Tait's ‘Nat. Phil.’ ed. 2, Appendices.

† Cf. ‘Baltimore Lectures,’ Appendix G, and Prof. Lamb's ‘Hydrodynamics.’

On board the yacht Helmholtz reports\* that "It was all very friendly and unconstrained. Thomson presumed so much on his intimacy with them that he always carried his mathematical notebook about with him, and would begin to calculate in the midst of the company if anything occurred to him, which was treated with a certain awe by the party. How would it be, if I accustomed the Berliners to the same proceeding? . . ."

The subject of fluid dynamics in all its branches had always great attractions for Lord Kelvin, doubtless in part owing to his association with the naval architects of the Clyde during the modern evolution of ship-building; applications to the resistance to the motion of ships, the phenomena of waves and wakes, propulsion by screws, and such like, were never far from his thoughts. Even in his latest years he continued to write abstruse mathematical papers on theoretical hydrodynamics with an energy and facility which were the wonder of younger men.

It was in the prosecution of this subject of the reactions of moving liquid on immersed solids, that one of his most daring developments arose, such as perhaps would hardly have occurred to a mathematician more circumspect about his formal logic. This was the application straight off, in Thomson and Tait (1867), of the generalised Lagrangian dynamical method to the dynamics of solids immersed in liquid, which proceeded by entirely ignoring the liquid once the formula for the total energy had been determined in terms of the motion of the solids. It seems that Lord Rayleigh, and afterwards Boltzmann, had early called his attention to the need for verification of this procedure; and in the German translation (1871, p. 294) a proof by means of the Principle of Least Action, on lines that had been suggested by Boltzmann, is supplied by Thomson himself. Kirchhoff had already dealt with an extension of one of Thomson's special problems in illustration, in a somewhat similar manner in 1869.† In a footnote Thomson promises with characteristic confidence that the second volume of the 'Treatise' (which was never prepared) will contain a complete discussion, on the basis of Hamilton's principle, of the dynamics of cyclic motion. Something of this appeared later in the 'Phil. Mag.'

A thoroughgoing treatment ultimately came in the second edition of Thomson and Tait in 1879, but the foundation on Hamilton's principle was dropped. The theory of the elimination of co-ordinates, such as those of the individual particles of the fluid—Ignorance of Co-ordinates, as he called it—

\* 'Life,' p. 287.

† 'Abhandlungen,' p. 176. But in a paper on "The Motion of Free Solids through a Liquid," 'Proc. R. S. Edin.,' 1870-1, reprinted as an Appendix to 'Baltimore Lectures,' 1904, Thomson starts off by quoting from his private journal, of date January 6, 1858, the equations of 'Eulerian' type of the motion of a solid in liquid, expressed by the principles of momentum in terms of the six components of the translational and rotational impulse of the motion, which are themselves given as gradients of the function expressing the kinetic energy. This idea of 'impulse' was developed formally in the memoir on Vortex Motion of 1868. Cf. Prof. Lamb's 'Hydrodynamics.'

opened up, when thus generalised, an entirely new domain in the application of dynamics to general physics. In the ordinary Lagrangian dynamics the masses of which it treats are characterised by configuration and inertia; on the wider theory, they may also possess permanent momenta of spinning or other cyclic motions. By introducing this third endowment the horizon of physical application and dynamical elucidation is obviously very widely extended. The theory had been already published independently by Routh in 1877, in his Adams Prize Essay on 'Stability of Motion,' in more perfect form than Thomson's; for he had reduced the analysis into dependence on a single function, which he called the modified Lagrangian function of the system. The translation of the general theory, as thus compactly expressed, into relation with the principle of action and general Hamiltonian dynamics, was not difficult.\*

At a later date (March 1884) Helmholtz got into the same subject, the modified Lagrangian function, in a series of papers on the Statics of Monocyclic and Polycyclic Systems, with application primarily to concealed cyclic motions such as might illustrate one possible aspect of the latent thermal energy in thermodynamics, or perhaps rather of the intra-molecular part of it. His treatment, which was identical with Routh's, culminated in a beautiful memoir in 'Crelle's Journal' (1886) on the physical significance of the principle of Least Action, in the course of which the idea of reciprocal theorems introduced by him long before in connection with acoustical problems, and developed in other directions more particularly by Lord Rayleigh and Maxwell, was placed on the widest foundation, in a manner which, however, was familiar to Hamilton himself in his own narrower physical range.

Another classical problem in mathematical physics in which new developments were included in the second edition (1883) of Thomson and Tait was that of the forms of a steadily rotating mass of gravitating fluid. Thus § 778 begins: "During the fifteen years which have passed since the publication of our first edition we have never abandoned the problem of the equilibrium of a finite mass of rotating incompressible liquid. Year after year, questions of the multiplicity of possible figures of equilibrium have been almost incessantly before us, and yet it is only now, under the compulsion of finishing this second edition of the second part of our first volume, with hope for a second volume abandoned, that we have succeeded in finding anything approaching full light on the subject." Then follow eleven propositions, stated without proof, arranging in most ingenious manner the known forms, so as to trace the order of transition between the successive configurations of stable and unstable steady motion, as the circumstances are gradually changed. In fact the problem was left ready for its next stage of development which came two years later (1885) in Poincaré's classical memoir, in which, building on the stationary property of the modified Lagrangian function or kinetic potential, the transitions between stabilities and instabilities in steady motion were made amenable to processes of

\* Cf. 'Proc. London Math. Soc.,' March 1884.

continuous graphical representation. For the subsequent developments by Sir G. H. Darwin and others, with important bearings on problems of cosmical evolution, reference may be made to the last chapter of Prof. Lamb's 'Hydrodynamics.'

The evolutionary and tidal problems treated near the end of the original edition had in fact meanwhile been made his own by G. H. Darwin, so that it was natural that his assistance should be sought to bring the new edition up to the existing state of knowledge. In particular in an appendix, Part II, pp. 505-17, his beautiful graphical discussion of the secular effects of tidal friction is reproduced. The problem as to whether the waste of energy by terrestrial tidal friction came from the Earth or the Moon had been given up long before by Airy as intractable, a decision which, however, stimulated J. Purser, a close friend of Lord Kelvin and of his brother, to its definite and concise solution by combining the necessary conservation of the angular momentum with the frictional diminution of the mechanical energy.\* The graphical treatment of the subject on the basis of these two relations had it seems been suggested by Lord Kelvin, with results which in Darwin's hands (1879) originated a new branch of astronomy, the dynamical theory of the evolution of planetary systems.

This discussion of cyclic systems, when energy is dissipated through friction, led† also to the fundamental distinction between ordinary and secular stability. "The gyrostatic forces which we now proceed to consider may convert instability into stability as in the gyrostas [with two degrees of freedom] *when there is no dissipativity*; but when there is any dissipativity, gyroscopic forces may convert rapid falling away from an unstable configuration into falling by (as it were) exceedingly gradual spirals, but they cannot convert instability into stability."

It would seem that one of the main endowments that go to the making of a mechanical engineer is an acquired sense of the inertia of matter, an instinctive feeling of what may be expected of great moving masses and the limits within which they may be controlled, whether they are ships straining on their cables, or fly-wheels whose normal function is in steadying rather than disturbing motion. This gift, which differs from the faculty of formal dynamical calculation as the instinct of a homing pigeon differs from the trials of a wanderer finding his way with a compass, was possessed in supreme degree by Lord Kelvin. It seems, in fact, to have been reserved for him to invent a distinctive name for the principle of rotatory momentum, of which the beginnings were already known to Newton though the bearings of the constancy of rotatory momentum in a self-contained system gradually came out into clearer light in the hands of his successors. It was expounded by d'Alembert how the spin of the Earth on its axis kept the direction of that axis fixed, except as regards the precessional motion definitely due to the

\* 'Brit. Assoc. Report,' Belfast, 1874, pp. 22-24.

† Thomson and Tait, Edit. 2, § 345<sup>v</sup>; cf. also Lamb's 'Hydrodynamics,' § 197.

torque of solar and lunar attraction on the equatorial protuberant matter—just as the overhanging weight of a spinning top produces precession of its axis round the vertical. The famous corollary seemed comparatively new when Laplace developed it, that it is possible to determine a plane of reference—his invariable plane, so called—in the Solar system, which must remain absolutely fixed in direction throughout all time, that namely of the resultant rotatory momentum. But instead of rotatory momentum these writers were accustomed to speak of rate of description of areas, in extension of the language of Kepler and Newton which was appropriate enough to a single planet travelling round the sun. When, however, we pass from the discrete planets of astronomy to the continuous spinning solids of dynamics, this terminology is nearly as unwieldy as the mathematical formulas themselves, and, worst fault of all, is quite unsuggestive. Though Poinso't's reform of procedure in statics, by introducing the idea of a turning couple or torque alongside that of a force, had undoubtedly much to do with the result, the dynamics of rotation began to assume a far more tractable form when expressed in terms of the incisive language developed in 1867 in Thomson and Tait's '*Natural Philosophy*.' The remark of Helmholtz on the difficulty of translation of the new terms in the German edition may be recalled.

This dynamical instinct was not content to rest with a reconstitution in more formal terms of the principles of rotatory motion. To cultivate dynamical ideas further by actual acquaintance with the rotatory inertia of spinning masses, Thomson converted Foucault's gyroscope into a gyrostat, which may be considered as a fly-wheel with rapid spin impressed on it, isolated and protected inside a frame or case so that it could be manipulated in many ways, while this rotatory momentum would in the absence of friction remain a permanent static possession, effectively of the very essence of the gyrostatic system. The stiffness as regards direction, as shown by the wriggling resistance that such a body opposes to merely altering its orientation in space, opened up a new and fascinating domain in dynamics. In the second edition of Thomson and Tait (1881, p. 396), a section is introduced, with diagrams, illustrating some of the extraordinary ways in which these gyrostats can stand, balanced on an edge and in other strange positions, and refuse to stand in positions which are easily assumed by masses devoid of the concealed rotatory momentum. Such phenomena were to acquire fundamental philosophical significance in more than one direction, including the introduction of permanent latent motions into general dynamical theory referred to above, and the gyrostatic model of an optical æther which will be described presently.

As experimental illustrations of the perverse effects of internal spin, the gyrostats were already of long standing, and their mysterious behaviour constituted one of the puzzles that greeted visitors to the laboratory at Glasgow. Already during his visit at Easter 1864, Helmholtz reports home to his wife an experience which illustrates another advantage of the enclosing case. "Thomson's experiments, however, did for my new hat. He had thrown

a heavy metal disc into very rapid rotation, and it was revolving on a point. In order to show me how rigid it became by its rotation, he hit it with an iron hammer, but the disc resented this, and it flew off in one direction and the iron foot on which it was revolving in another, carrying my hat away with it and ripping it up."

In 1865, the principles of clock escapements and compensations began to occupy Thomson's attention, and after many efforts he reported to the Royal Society in 1869 on a standard astronomical clock which he had constructed, with strict attention to dynamical principles, and erected on a firm foundation in the hall of his house at the University of Glasgow, where it still remains. It does not appear that the promised future reports on the performance of this type of clock as compared with the usual observatory clocks were ever made. But long subsequently, in an address delivered at Manchester on watches and chronometers, he adverted, with some dissatisfaction, to the fact that for the customary expenditure of a few shillings, one could only procure a watch which with ordinary rough treatment would keep time to one part in ten thousand, or perhaps, with care, one in a hundred thousand.

He had communicated to the Royal Society in 1856 a formal memoir on another subject which occupied much of his later thought, the Mathematical Theory of Elasticity; in this paper the kinematic analysis is of very general type; but doubtless one of the aims was to reform and purify the theory by basing the subject on the appropriate thermodynamic function, the free or Available Energy, which had been established by him the year before (*supra*, p. xlvii), as the proper physical expression of Green's mathematical principle. This was followed in 1863 by a mathematical application, difficult for that time, to the stresses excited by rotation in elastic spheroids and in shells containing incompressible perfect liquid, with a view to the bearing of the results on the question of the rigidity and internal constitution of the Earth as tested by the amount of the astronomical precession and nutations. This application belonged to the geological and evolutionary part of his work, and also included considerations relating to shift of the Earth's axis, and the change of the length of the day owing to tidal and other causes; it was reprinted in 1878, but with corrections arising from the criticism of Newcomb and others, who had persuaded the author that he had actually himself underestimated the directional persistence of the rotating fluid interior.

In a Presidential Address to Section A of the British Association, Glasgow, 1876, an account was given of this pre-occupation with the Earth's rotation and rigidity, precession and nutation, tides and monsoons, meltings of polar ice, etc. The opening paragraphs of this Address express his vivid impression of all that he had just seen in a visit to the Philadelphia Exhibition (followed in later years by numerous other Transatlantic visits) of the great undertakings in organised scientific work that were being carried through in America. He includes a description of his experience with the telephone, then nascent,



which excited his admiration (as it did that of Helmholtz) as a practical and definite embodiment of the fundamental doctrine which was illustrated in another phase by his own tidal developments—the Fourier harmonic analysis of oscillatory motion.

Since his return from America the criticism of Newcomb, above mentioned, had focussed his thoughts. As he explained in the Address, he had not yet begun in 1862 to ponder over the stabilities of vortices and other configurations of spin. The state of the case regarding terrestrial physics, as now amended, is shortly this :—"The hypothesis of a perfectly rigid crust containing liquid violates physics by assuming preternaturally rigid matter, and violates dynamical astronomy in the solar semi-annual and lunar fortnightly nutations; but tidal theory has nothing to say against it. On the other hand, the tides decide against any crust flexible enough to perform the nutations correctly with a liquid interior, or as flexible as the crust must be, unless of preternaturally rigid matter." The results of the mathematical investigation on the precession of a hollow spheroid filled with liquid, which thus restricted the argument to rapid nutations, were given in the Address, but his analysis has apparently never been published, though other investigators have since supplied the want. Passing on to the free wanderings of the terrestrial pole and the consequent slight changes in latitude, he insists that notwithstanding that Peters and Maxwell and others could find at that early time no periodic effect, yet the irregular changes that were noted must be in part real, because existing meteorological causes such as winds, the melting of polar ice, etc., are competent to produce displacement of from one-twentieth to one-half of a second of arc. He goes on to consider the tides resulting from such a displacement of the Earth's axis, which are quite sensible; in fact, their periodic components have since been sought for in the tidal records. He decides against the occurrence in past time of vast 'four hundred metre' tides recurring in three or four hundred days, such as would be started by a geological convulsion involving sudden elevation of one octant of the Earth by about that amount with subsidence of other regions; but he then saw no reason why the polar axis should not have gradually travelled in the course of ages, in close company with the axis of inertia, through many degrees to its present position. This remarkable Address closes with a consideration of the causes of a possible diminution of the Earth's period of rotation such as Lunar Theory seemed to demand; it was some time later that he detected unexpectedly a quite sensible thermodynamic acceleration due to the diurnal lag of the barometer behind the Sun. But in any brief abstract it is quite impossible to summarise these activities. The Report of this Meeting (1876) records merely the title of a paper 'Physical Explanation of the Mackerel Sky,' which went on lines now familiar in meteorology, namely, interfacial wave-action due to cross currents rubbing over one another. He also reported again on his astronomical clock (*supra*, p. lxiii) still with hope, but results had been delayed by unfortunate choice of materials and construction for



1877

Yours very truly  
William Thomson



the compensated pendulums. At this very brilliant meeting of the British Association he read no less than eleven papers on the most varied subjects, and a long analytical report on tidal observations (pp. 275-307), not to mention other papers and reports partly inspired by him, in addition to the Presidential Address above quoted.

One of his striking mathematical achievements of a later date (the vortex motion period) was the demonstration that when a hollow ellipsoid of revolution filled with perfect liquid is set into bodily rotation, the motion of the liquid is stable only when the cavity is of the oblate kind. In illustration of this prediction he had hollow gyrostats made, which by aid of some skill could be set spinning bodily along with their liquid contents; the oblate one behaves as an ordinary gyrostat, but the prolate one, as soon as the orientation or the steady maintaining torque of the spinning cord is altered, makes a few violent wriggles and subsides by turbulent break up of the rotation of the liquid, which occurs the more rapidly the greater the spin it has acquired.

In the later years, in pursuance of elastic theory, much attention was devoted to the early view of optical double refraction and reflexion which ascribes to the æther the vibratory properties of a solid body. These properties were exactly specifiable as above by the function representing available energy, in the manner first employed by Green, to whom was due the first definite idea that the energy function provided the criterion of the precise amount of complexity that it was permissible to introduce in continuous elastic phenomena. For many years Thomson struggled hard, in successive papers full of brilliant subsidiary results, to bend somehow the elastic solid theory so that it might be forced into compliance with the very various conditions imposed by the optics of both isotropic and crystalline media. Sometimes he seemed to come near to success. But success was achieved only when he cast aside the idea of solid elasticity, and betook himself to the help of the anomalous elastic reaction belonging to his gyrostats, in the form of resistance to rotation rather than deformation. But it is of no use to this end merely to build up a model of a medium filled with spinning flywheels; the reaction to rotation would then be too complex. Each such flywheel is dynamically a directed element; if their axes are distributed at random, their primary effects cancel each other, while if there is a preponderance of the axes to any side, what they illustrate is a directed physical influence on the medium, of the same sort as (but not identical with) Faraday's influence of magnetisation on light. To simulate pure static elasticity by means of a gyrostat, it is necessary to arrange that a rotatory displacement produces a restoring torque directly proportional to the displacement, instead of to its velocity. The solution of the problem, mentioned earlier in the same year to the Electrical Engineers (*infra*), was explained in a communication in the *Comptes Rendus*, September 16, 1889, "On a Gyrostatic Adynamic Constitution for 'Ether,'" The constraints on the framework, itself

of the original Foucault gimbal type, that are necessary to make the static angular momentum of a gyrostal react in this simple way, would require some space to describe; for though Lord Kelvin's dynamical nomenclature has brought non-mathematical explanation into effective grasp, it can never be quite easy. It may suffice to say that just the same device allows a horizontal spinning flywheel to steady the rolling of a boat, by introducing a restoring torque of direct elastic type proportional to the angular deviation from the vertical.

The result thus reached in the elastic theory of the æther had been, however, in the abstract sense anticipated. This type of medium, operating by rotational stiffness arising from intrinsic internal rotation, was, in fact, a mechanical model of a mathematical æther introduced into optics nearly fifty years before by MacCullagh, but repudiated at the time, except by Rankine, on the very ground that it behaved in a way that an elastic solid could not do. By a mathematical æther is here meant a medium specified by its potential energy function alone, without any attempt at providing a mechanical model of the detailed working of the medium that is thus completely determined mathematically in the form of that function. The gyrostatic model is also identical, in the same mathematical sense, with the electrodynamic æther of Clerk Maxwell. In this way it has come to pass that by making a model, with ordinary matter, of an elastic medium that has not the properties of ordinary matter, Lord Kelvin has vindicated to many minds, if not entirely to his own, the power and cogency of the impalpable procedure of mathematical analysis which can reach away without effort from the actual to the theoretically possible, and thus, for example, make a mental picture of an æther which is not matter for the simple reason that it is something antecedent to matter. This may be taken to be a partial view, so it is well to offer direct support of it by a quotation from the Presidential Address of January 10, 1889, to the Institution of Electrical Engineers, an address which one may venture to think was equal in fundamental physical suggestion to any of the great achievements of his early years:—"So that I do not admit that it is only playing at theory, but it is helping our minds to think of possibilities, if by a model, however rough and impracticable, we show that a structure can be produced which is an incompressible frictionless fluid when no gyrostatic arrangement is in it, and which acquires a peculiar gyrostatic elasticity or rigidity as the effect of introducing the gyrostats into these squares." Later on he proceeds:\* "Thus, upon this solid, the effect of a constant couple is not to produce continued rotation, but to produce and balance a constant displacement, and that balance may last for any time, however long, if the rotational moment of momentum of the flywheel is but great enough." The last sentence implies the essential limitation of the model. This persistence of the steady balance demands continually increasing angular displacement of the axis of the gyrostal, so that it could

\* 'Math. and Phys. Papers,' vol. 3, p. 509.

not last for ever without some mechanism for recovery of direction; but if the movements are restricted to be vibratory or merely alternating, the model is adequate, and by taking its rotational momentum to be great enough the period of the alternation may be made as slow as may be desired, even so as to include an analogy of the cyclic field of a magnet lasting permanent for any assigned time.

The two immense branches of profound physical investigation, optical and electrical science, thus meet and fuse together. Their approach can be conducted in two ways; it may proceed from the side of optics by the method of MacCullagh, with its self-consistency finally justified by Lord Kelvin's model, when that method is expanded so as to include the application to disturbances of the æther that are not simply vibratory; or it may proceed, as it did historically, from Maxwell's invention of a mathematical æther capable of accounting for electric phenomena, by the mathematical verification that its vibratory properties are exactly those of light and radiation.

The rotational rigidity of æther, thus illustrated, did not, however, console Lord Kelvin, for he could not see how bodies can be free to move through the medium. It is true that he puts it that he does not see why magnets attract each other and electrified bodies attract each other; but it is really the mechanism of the free mobility that he is in quest of, for the forces are determinate by the principles of dynamics, and could not be otherwise, whatever kind of mobility there might be.

In the Address just mentioned, quoting from his paper of 1847 on an elastic solid analogy, he states with reference to its last sentence (*supra*, p. xii), written as he remarks twenty-eight days after he had taken up the duties of his professorship at Glasgow:—"As to this sentence I can now say, what I said forty-two years ago—*must be reserved to a future paper*. I may add that I have been considering the subject for forty-two years—night and day for forty-two years . . . the subject has been on my mind all these years. I have been trying many days and many nights to find an explanation, but have not found it." But he adds in a footnote a reference to a paper just written, May 1890,\* in which the *lacuna* is filled. There in Sec. 47, p. 465, in explaining the limitations of this æther, rotationally elastic in a way which can be illustrated but need not be specified, he adds:—"All this essentially involves the consideration of ponderable matter permeated by, or imbedded in, ether, and a *tertium quid* which we may call electricity, a fluid go-between, serving to transmit force between ponderable matter and ether, and to cause by its flow the molecular motions of ponderable matter which we call heat. I see no way of suggesting properties of matter, of electricity, or of ether, by which all this, or any more than a very slight approach to it, can be done, and I think we must feel at present that the triple alliance ether, electricity, and ponderable matter is rather a

\* 'Math. and Phys. Papers,' vol. 3, pp. 450-465.

result of our want of knowledge and of capacity to imagine beyond the limited present horizon of physical science, than a reality of nature."

Looking back on this, however, one can see that the electron was not far off. These models, it can be held, now carry us further. Clearly if we could explain how one single atom is freely mobile through the æther, everything would be achieved; but the atom must be an ion and carry an electric field with it. There exists, it may be maintained, a satisfactory representation of how this electric field can travel in indissoluble attachment to a central nucleus—the whole arrangement called in 1894 an electron. But of the nature of the nucleus little more is yet ascertained, except that it is almost certainly isotropic as it was natural to assume, and can thus be representable as regards its influence at a sufficient distance by a spherical collocation of electricity; for all ordinary purposes of electrodynamics it remains, as then, a point-charge.

Mathematical analysis is the all-powerful resource that gets behind and away from all accidents of models and modes of visualisation in which our experience is necessarily set, back to the 'callow principles' as George Herbert called them. But however instructive it may be to revise our knowledge by its expression in terms of pure concepts free of all gross material implication, it seems safe to assert that it could never have been reached, in either of the ways mentioned above, without constant pre-occupation, mental or tangible, with the modes of working of dynamical models and illustrations.

It has been mentioned already (p. xlii) that Lord Kelvin's difficulties in representing radiation-pressure, with such models of electrons as he clung to, prevented him from appreciation of the modern thermodynamics of natural radiation. A recent attempt to persuade him to look into this matter elicited the following characteristic reply, in autograph, of date May 8, 1907:—"There are certainly very wonderful 'push and pull' forces in the action of light on movable bodies in high vacuum (and also in not very high vacuum, as shown in Varley's communication to Royal Society. 'Proceedings' of about 1871, demonstrating cathode torrent of 'negatively' electrified particles). I do not, however, think that there is any foundation for push and pull in Maxwell's ( $\alpha, \beta, \gamma$ ) formulæ, or in the ( $\alpha, \beta, \gamma$ ), (P, Q, R) of your leaves. There is great importance in all such experiments as those of Hull to which you refer, and those of Crookes at various times, and those of J. T. B., of which we are now hearing,\* and of Dewar's which I believe he is to show this evening.† Great revelations are, I believe, coming early. Yours very truly, Kelvin.—I hope to continue this verbally when I see you in the evening."

\* J. T. Bottomley, 'Roy. Soc. Proc.,' March 18, 1907, on localised radiometer repulsions between the gold leaves of electroscopes, etc.

† Sir J. Dewar, 'Roy. Soc. Proc.,' June 27, 1907, on the lower limit to the action of the radiometer.

In 1884 Sir W. Thomson delivered the well-known course of lectures on Molecular Dynamics and the Wave Theory of Light at Johns Hopkins University, Baltimore, after attending the meeting of the British Association at Montreal. The papyrograph unrevised report issued in December, 1884, by Mr. A. S. Hathaway, may justly be said to have reawakened, or at any rate strongly intensified, interest in the ultimate form of the problem of æther and radiation, both in this country and abroad. It seems fair to say also that the interest and value of the lectures arose largely from the unpreparedness of their author. As his audience of American physicists fed him from day to day with the more recent experimental and theoretical results relating to selective absorption, which were largely new to him, they had before them the spectacle, on which Helmholtz had laid stress (*supra*, p. lv), of one of the great minds of the century struggling with fresh knowledge and trying to assimilate it into his scheme of physical explanation, calling up all his vivid store of imagery and analogy to aid. His auditors at the time, and his readers afterwards, thus must have considered the lacunæ and difficulties as their own personal problems in which they were assisting. Perhaps no exposition in physical science so vivid and tempting has ever been published; and for many years afterwards scientific activity in these subjects was strongly tinged by the Baltimore lectures, which transformed optics for the time from an affair of abstract mathematical equations into a subject of direct physical contemplation in close touch and analogy with the objective manifestations of ordinary dynamics.

In the preface to the authoritative edition of 1904, which in the twenty years' interval had grown to be a volume of some 700 pages octavo, Lord Kelvin in fact describes the object of the course of lectures as follows:—  
 "I chose as subject the Wave Theory of Light with the intention of accentuating its failures, rather than of setting forth to junior students the admirable success with which this beautiful theory had explained all that was known of light before the time of Fresnel and Thomas Young, and had produced floods of new knowledge, splendidly enriching the whole domain of physical science. My audience was to consist of professorial fellow-students in physical science; and from the beginning I felt that our meetings were to be conferences of co-efficients\* in endeavours to advance science, rather than teachings of my comrades by myself. I spoke with absolute freedom, and had never the slightest fear of undermining their perfect faith in ether and its light-giving waves; by anything I could tell them of the imperfections of our mathematics; of the insufficiency or faultiness of our views regarding the dynamical qualities of ether; and of the overwhelmingly great difficulty of finding a field of action for ether among the atoms of ponderable matter. We all felt that difficulties were to be faced and not to be evaded; were to be taken to heart *with the hope of solving them if possible*; but, at all events, with the certain assurance that there is an explanation of every difficulty though we may never succeed in finding it."

\* In the literal sense of the term.



He goes on to say that he had now, in 1904, virtually got to the bottom of the difficulties of 1884. He thinks, too, that in the wider field of æthereal phenomena *everything non-magnetic* can be explained "without going beyond the elastic-solid theory," but *nothing magnetic*. "The so-called electro-magnetic theory of light has not helped us hitherto: but the grand object is fully before us of finding comprehensive dynamics\* of ether, electricity, and ponderable matter, which shall include electrostatic force, magnetostatic force, electro-magnetism, electro-chemistry, and the wave theory of light."

His purely scientific activity from 1884 onwards hinged largely on the production of the definitive edition of these lectures, which, in terms of the remarks just quoted, had raised up in front of him all the difficulties in modern optical and general æthereal theory. The resulting volume, with its numerous insertions, including most of pp. 280-468, and the twelve Appendices occupying pp. 468-700, may take rank in fact as virtually Volume IV of the 'Mathematical and Physical Papers.' Among the vast array of new and recent material collected into the volume there may be mentioned the following: theory and observation on the opacity of air and gases, reflexion from diamond and from metals, his various attempts at elastic solid vibratory theories of the æther, rotation of the plane of polarization combined with double refraction, waves on water and in dispersive media with the residual disturbance they leave behind, waves raised by wind or by ships, the total mass of the material universe, various theories of electrons or electrions as he preferred to call them; also much regarding molecular tactic of crystals and the resulting dynamics, this time on a Boscovichian foundation. The Royal Institution Lecture of 1900 on 'Nineteenth Century Clouds over the Dynamical Theory of Heat and Light' is also included; these difficulties he there reduces to two: the difficulty regarding the motion of matter through æther, which he thinks is "not wholly dissipated," and the difficulty about the frittering away of the energy of gaseous molecules among their numerous periods of free vibration, which he solves in what may possibly be held to be the natural way, by denying the proofs.

An estimate of Lord Kelvin's influence on modern geology has been contributed for this Notice by his lifelong friend, Sir Archibald Geikie:—

"Throughout his life Lord Kelvin took much interest in the progress of geology. From the year 1844 onwards for some eighteen years, he watched with increasing impatience the spread of the doctrines of the Uniformitarian School, which reached the height of its influence about the middle of last century. At length in the year 1862 he broke silence on the subject, declaring the doctrines of that school to be opposed to physical laws. Three years later he gave greater emphasis to his antagonism by publishing a short paper with the uncompromising title, 'The Doctrine of Uniformity in Geology briefly refuted.' Again in 1868 he returned to the attack and brought forward additional lines of argument in support of his charge that British

\* Cf., however, pp. xi, xviii-xxiv, lxv, *supra*.

popular geology stood 'in direct opposition to the principles of natural philosophy' and required 'a great reform.'

"It was one of the accepted tenets of the Uniformitarian School that the range of past time available for the explanation of the phenomena of geology was unlimited. But by arguments drawn from the origin and age of the sun's heat, the internal heat and rate of cooling of the earth, and the tidal retardation of the earth's rotation, Kelvin fixed limits to the possible age of our planet. At first he maintained that this age could not be less than twenty millions of years nor more than four hundred millions. In his latest writings on the subject he restricted the time to between twenty and forty millions.

"His papers have given rise to a prolonged controversy and no final agreement has yet been reached. But these papers have profoundly influenced the course of modern geological speculation. They roused geologists from their comfortable belief in the limitless ages of the past, and led them to revise their estimates of the value of geological time. Lord Kelvin's insistence greatly helped to tone down the extreme uniformitarian views which were in vogue half a century ago. Even those geologists, palæontologists, and biologists who most keenly dispute the validity of the arguments whereby he sought to compress the antiquity of the globe within limits that seem too narrow for the evolution of geological history, must admit that in turning the brilliant light of his genius upon this subject he did a notable service to the progress of modern geology."

Little has been said here with regard to Lord Kelvin's masterful and most effective preoccupation with the development of modern electric engineering, which has now almost completed the transition from the age of steam to the age of electric power. In this new branch of applied science, his active perception of the essentials of progress assumed the form of generalship: most of the details of progress naturally came from others, but he was ready always to emphasise the salient problems, and to acclaim, early and enthusiastically, such nascent inventions as would be pertinent to their mastery. An example is afforded by the emphasis with which he hailed the invention of the original Faure storage cell or accumulator,\* which promised to supply the improvements (including the subdivision of a large storage battery to play the part of a step-down transformer, not yet practically effective) then necessary for economical development of the electric generation of power. This subject came particularly to the front in his Presidential Address in 1881 at York to the Physical Section at the Jubilee Meeting of the British Association, "On the Sources of Energy in Nature available to Man for the Production of Mechanical Effect," which almost repeats the title of his early paper of 1852, but is this time concerned with the practical utilisation of these sources, now rapidly ripening, whereas the earlier discussion related to their philosophical detection and estimation. In this Address, after referring to Siemens'

\* 'Brit. Assoc. Report,' 1881, p. 526.

suggestion, three years previously, of the electrical transmission at high potential of the power of Niagara Falls, itself resting, as he remarks, on Joule's early experimental discovery that in an electromagnetic engine as much as ninety per cent. of the energy of the driving current can be utilised, he proceeds to summarise his own conclusions regarding economy of transmission over long distances, as communicated in the form of evidence to a Parliamentary Committee two years before. The brief paper, now classical in electro-technics, then communicated,\* "*On the Economy of Metal in Conductors of Electricity*," is an early notable instance of the blending of economics with exact physics: the solution of the problem "would be found by comparing the annual interest of the money value of the copper with the money value of the energy lost annually in the heat generated in it by the electric current. The money value of a stated amount of energy had not yet begun to appear in the City price lists." He shows that the gauge to be chosen for the transmitting conductor does not depend on its length, but solely on the strength of the current to be employed. He was much concerned also in the early evolution of dynamos (the term had been introduced by him about this time as a contraction for dynamo-electric machine), the designing of which was to become entirely effective a few years later by means of the graphical methods introduced by Hopkinson. Perhaps the earliest domestic installation of electric lighting in this country was the experimental one which he established in his house at the University of Glasgow; while one of the early public installations was the one, still in operation, which he presented, in connexion with the celebration of the six hundredth anniversary of the foundation of that most ancient house, to his College in Cambridge, which had been able, under new statutes, to re-elect him to the Fellowship that he had vacated long before on his marriage.

The introduction of heavy currents and voltages in engineering required the provision of suitable instruments of measurement. This was always a congenial task: his graded series of current-weighers or ampere-meters, and of volt-meters—embodying those theoretical principles of adequate support free from constraint or strain, in mechanical design, on which he always insisted, to the great improvement of general practice in such matters—have proved to be of fundamental service wherever exact measurement is essential.

His interests ramified into all departments of human activity: even his physical writings were often relieved by play of allusion to literature and history. In his later years he took an active and zealous part in political affairs, and attended regularly the sittings of the House of Lords. In his undergraduate days he was one of the founders of the Cambridge University Musical Society, playing the French horn at its opening concerts in 1843. Later he published some observations† on the beats of imperfect harmonics of simple tones, tending to a conclusion different from that of Helmholtz which referred the beats to combination tones.

\* 'Brit. Assoc. Report,' 1881, pp. 526-8.

† 'Roy. Soc. Edin. Proc.,' 1878.

All this activity implied a robust constitution. As an undergraduate at Cambridge he found time to take a keen interest in manly sports, rowing in the Peterhouse boat, which had second place on the river, and winning the Colquhoun Sculls, then, as now, one of the main objects of athletic ambition. Afterwards he was expert at curling until a serious accident on the ice stopped the pursuit, and left him slightly lame for life. His subsequent yachting and cable-laying experiences have been already referred to.

The general impression produced, at first sight, by the four volumes, containing the collected scientific papers up to 1860, might well be a somewhat vague notion of desultory, though profound, occupation with the ideas that were afterwards to be welded by more systematic expositors into our modern theoretical knowledge of mechanical and electrical and optical philosophy. At first glance, the exposition in characteristically practical terminology might even suggest that these papers were concerned with the engineering achievements by which he is most widely known, as much as with new theoretical foundations for physical science. Closer attention has compelled the conclusion that the results of his activity in the early period from 1845 to 1856 are perhaps unique in modern scientific annals; at any rate, there can have been few parallels since Newton and Huygens and their great predecessors. It is said that Lagrange qualified his profound admiration for the genius of Newton by the reflexion that only once could it be given to a mortal to have a system of the stars to unravel. Somewhat in the same way one might imagine the reflexion of a seer of the future, that it can hardly be given again to a man of genius to have, in his first dozen years of creative intellectual activity, the ideas and discoveries of a Carnot, a Faraday, and a Joule, to interpret and develop for mankind.

His only peer in general physics in those early days, as also later if we exclude his own disciples, was perhaps Helmholtz. They began their careers of investigation about the same time, but at first their paths did not lie much together. For in his early years Helmholtz's professional work was that of a physiologist, though in the essay on the Conservation of Energy he revealed, in 1847, his true bent as a leader in the exploration of the underlying principles connecting the different departments of the fundamental science, general physics. By the time this famous essay came into Thomson's hands in 1852, he had himself travelled, with Joule's assistance, as far as it reached, if we except some special applications; but much more, he had in fact already dug down, on the inspiration derived from Carnot, far into the true foundations of the doctrine of Energy as available and recognisable to man, evolving from it ideas now familiar but then of revolutionary significance, as regards both dynamical science and cosmic evolution, of which no one up to that time had any definite notion. The saving virtue of physical or any other genuine science is that the most essential discoveries of one generation become worked up so as to be obvious and almost axiomatic to the next. The charm of the study of scientific history is thus to trace the beginnings of creative ideas, to

see how slight sometimes was the obstacle that delayed the discovery of a new field of knowledge ; though here the temptation to read back our own refined knowledge into the past lays many snares. In no part of science is this interest greater than in the doctrine of Available Energy ; the generality of outlook, leading to recasting of the fundamental ideas regarding physical force and power, which was secured by Thomson away back in the fifties, is on the least favourable view a matter for wonder.

In the years following, the powers of Helmholtz were concentrated largely on his great task of the exploration of the physical foundations of the activity of the senses, a subject of fundamental importance because they supply our only outlook into the external world ; while Thomson's efforts were employed in the problem, then urgent and preparatory to Maxwell, of the dynamical interpretation of the ideas of Faraday, and in the creation of the fundamental science above referred to, which constitutes Thermodynamics in its widest sense, the all-pervading doctrine of Available Physical Energy to which it seems appropriate that Rankine's name Energetics should belong. In later days of close friendship their fields of activity had much in common, Helmholtz apparently often brooding over, and developing into fuller and more varied aspects, fertile points of view, such as the influence of wind and surface-tension on waves, and the generalisation of dynamics by the inclusion of latent cyclic motions, that had been already thrown off in more summary fashion by his colleague. On the institution of the Helmholtz memorial medal, the first award was to Lord Kelvin.

In a letter to Tait in 1876,\* who was preparing a biographical notice for 'Nature,' Helmholtz had given an estimate of the work of his friend at that period. "His peculiar merit, according to my own opinion, consists in his method of treating problems of mathematical physics. He has striven with great consistency to purify the mathematical theory from hypothetical assumptions that were not a pure expression of the facts. In this way he has done very much to destroy the old unnatural separation between experimental and mathematical physics, and to reduce the latter to a precise and pure expression of the laws of phenomena. He is an eminent mathematician, but the gift to translate real facts into mathematical equations, and *vice versa*, is by far more rare than that to find the solution of a given mathematical problem, and in this direction Sir William Thomson is most eminent and original. His electrical instruments and methods of observation, by which he has rendered, amongst other things, electrostatical phenomena as precisely measurable as magnetic or galvanic forces, give the most striking illustration how much can be gained for practical purposes by a clear insight into theoretical questions ; and the series of his papers on thermodynamics, and the experimental confirmations of several most surprising conclusions deduced from Carnot's axiom, point in the same direction."

We have seen the hints and principles thrown out by Thomson in such profusion fructify in patient development by other great investigators, so that

\* 'Nature,' vol. 14, 1876, p. 388.

it would be difficult to name a branch of modern physical science in which his activity has not been fundamental. In one phase of his thought, it becomes cosmical and transcends experimental aids. All through life his ideas were wont to range over the immensities of the material universe, reaching back to its origin and onward to its ultimate fate. In his youth he established the cardinal principle of inanimate cosmic evolution, as effected through the degradation of energy, which determines the fate of worlds, and is the complement of the principle of evolution in organic life which came to light at about the same time. In another aspect of this principle, asserting that the trend of available energy must always be downwards, it has developed into the key to the course and the equilibrium of voltaic and chemical change, and to all other branches of physical knowledge in which the atomic nature of matter is the pervading influence. The greatness of the revolution thus effected in physical science, and in its industrial applications which are in strict relation to this available energy, requires no emphasis. The magnitude of the advance brought by the mere enunciation of the principle of dissipation is to be measured by the very inevitableness of this law to our present modes of thought; it is difficult now to recognise the limitations that must have belonged to the time when its formulation caused such surprise and wonder.

At the end of his strenuous career his thoughts reverted again to these problems of the origin and destiny of material things. Novel considerations were brought to bear, with intellectual vigour appropriate to youth, to demonstrate even the finiteness of the material universe—such, for example, as the darkness of the firmament and the moderate magnitude of the relative velocities of the most distant stars. In the last weeks he pondered over the remote history of our own planet, and reasoned with striking force and lucidity, as may be read in a posthumous paper, on the antiquity of its continents and oceans, reaching back possibly to the time when the Moon separated from the Earth.

In this Notice the chief aim has been to set out a connected historical view of the course of Lord Kelvin's scientific activity and its relation to his contemporaries. No attempt has been made to describe the charm of his personality. That has been recognised long ago by the whole world; for many a year the ordinary restrictions of nationality have had little application to him; he has been venerated and acclaimed wherever scientific investigation is appreciated. No instance in his long career can be recalled in which he asserted for himself any claim of priority in intellectual achievement; rather his attitude has always been to show how much he had learned from his colleagues, and how much he expected to derive from them in the future. In this regard there is just time to interpolate an extract from the fine appreciation by Lord Rosebery, his successor in the chancellorship of the University of Glasgow, delivered in his installation address\* :—"In my

\* 'The Times,' June 13, 1908.

personal intercourse with Lord Kelvin, what most struck me was his tenacity, his laboriousness, his indefatigable humility. In him was visible none of the superciliousness or scorn which sometimes embarrass the strongest intellects. Without condescension, he placed himself at once on a level with his companion. That has seemed to me a characteristic of such great men of science as I have chanced to meet. They are always face to face with the transcendent mysteries of nature. . . . Such labours produce a sublime calm, and it was that which seemed always to pervade Lord Kelvin. Surely, in an age fertile in distinction, but not lavish of greatness, he was truly great. Individualism is out of fashion. . . . But great individualities such as Lord Kelvin's are independent of the pressure of circumstance and the wayward course of civilisation."

It is unnecessary to attempt any list of the distinctions and awards which came to him in the course of years; it suffices to say that there was probably no honour open to a man of science that was not at his disposal. Abundant personal record is and will be available in appreciations by his colleagues, who were all his friends; for example in the masterly estimate by G. F. FitzGerald contained in the memorial volume reporting the proceedings in celebration of the Jubilee of his Professorship at Glasgow in 1899. In deference to the strikingly unanimous desire of his countrymen of all classes, and amid touching tributes from his colleagues in other nations, he was laid finally to rest in historic ground, on December 23, 1907, alongside his great exemplar Sir Isaac Newton, in Westminster Abbey.

J. L.

**OBITUARY NOTICES**  
**OF**  
**FELLOWS DECEASED.**  
*(Continued.)*



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## P. J. C. JANSSEN, 1824—1907.

PIERRE JULES CÉSAR JANSSEN was born in Paris on February 22, 1824. Son of a musician, grandson of an architect, both distinguished, an artistic career was arranged for him, and he began the study of painting with great diligence, but he was so forcibly attracted by physical science that he eventually took up his studies in that direction, always, however, retaining a great taste for art. He was, to a large extent, self-taught, as his father lost his property; Janssen for some years supported himself by working in a bank and in giving private lessons. Every spare hour, however, was spent at the Sorbonne in following the lectures of Cauchy, Chasles, Le Verrier and others, and on Sundays he studied at the Conservatoire. In 1852 he obtained the Degree of Licentiate of Mathematical Science, he was répétiteur at the Lycée Louis le Grand in this year, and, in 1855, won the diploma of Licentiate of Physical Science, after which he eventually took his degree at the University.

In 1857 the Minister of Public Instruction, in spite of Janssen's lameness, which he owed to the carelessness of a nurse, put him in charge of an expedition to determine the course of the magnetic equator across Peru. He was accompanied by the two brothers Grandidier, his pupils. Alfred Grandidier became, subsequently, an explorer of Madagascar, and was made a Member of the Academy. Janssen unfortunately contracted fever in traversing the swamps and forests, and was obliged to abandon his measurements. For many months he was so seriously ill that the return to Europe could not be undertaken till the next year. On his return he took another teaching position at Creusot, and, while so engaged, he prepared his thesis for the Degree of Doctor of Physical Science. This dealt with a remarkable study of the eye, in which he demonstrated that the media of the eye possess the property of absorbing dark radiant heat, and only allow those rays to reach the retina which are necessary for vision. He obtained the degree on the strength of this in 1860; and it was Kirchhoff and Bunsen's discoveries at that time which deflected him from Ophthalmology to Spectroscopy, to which, in the main, the rest of his life was devoted. His spectroscopic studies began by enquiries into atmospheric absorption.

First a large dispersion was employed to study the solar spectrum at varying altitudes. He had already built a private observatory in 1862, on a belvedere on the top of his house in the Rue Labat (Montmartre). From 1862 to 1864 he was occupied with missions to Italy and the Alps in connexion with this work, to get the least density of atmosphere by observing at a high altitude. Eight days on the Faulhorn, in 1864, were enough to enable him to state that the telluric rays were much less visible at that elevation.

In the same year experiments were undertaken near Geneva for the same purpose. The spectrum of a large bonfire at Nyon was examined by a

spectroscope there and afterwards located in the tower of St. Peter's Church at Geneva, twenty-one kilometres away over the lake. The telluric lines were observed and that they were due to absorption by the atmosphere was strongly suggested; later work at La Villette ran them home to water vapour.

From 1865 to 1871 Janssen held the post of Professor of General Physics at the Special School of Architecture, but, as we shall see, he found time to continue his spectroscopic work and expeditions.

In 1867 he went to Trani, in Italy, to observe the eclipse of the sun, with special reference to the thickness of the reversing layer in the sun's atmosphere. He was in the Greek Archipelago with Fouqué at the time of the eruption of Santorin, where he observed the sodium and hydrogen lines in the flames from the lava. He ascended Mount Etna, where he detected the probable presence of water vapour in the atmospheres of Mars and Saturn. Also in 1867 he went to the Azores to make optical researches with Charles Sainte-Claire Deville; while crossing Spain and Portugal he spent some time in securing magnetical observations. In 1868 he observed the eclipse of the sun at Guntoor, in Hindustan, on behalf of the French Government, the Académie des Sciences, and the Bureau des Longitudes.

This was the occasion on which he discovered that by using a spectroscope the sun's surroundings and their chemistry could be observed without the intervention of an eclipse. During the eclipse he was struck with the great brightness of the lines, chiefly of hydrogen, which were visible, and it struck him that they ought to be visible at other times. The weather clouded after the last contact, so nothing could be done that day; but he rose at 3 A.M. the next morning, and, having arranged his apparatus in the way he had thought out, with a radial slip adjusted for C, he soon saw a bright line in prolongation of the dark C in the spectrum of the photosphere.

Referring to these observations in a letter to his mother on September 6, he wrote, "Je lis dans un livre fermé jusqu'ici pour tous . . ."

The French Government, recognising the importance of the discovery of the new method of sun observation, at once sent out to Janssen the Cross of the Legion of Honour. The Academy of Sciences awarded him the Lalande prize, quintupled in value, and further, at the suggestion of M. Dumas, struck a medal to commemorate the event.

A year afterwards, in 1869, Janssen suggested at the Meeting of the British Association at Exeter the use of two slits on a rotating spectroscope so that a complete image of the prominences could be photographed on a fixed plate. Here we have the germ of the idea which has since been utilised by both Hale and Deslandres with such success.

In 1870 there was an eclipse visible in Algeria, and in 1869 Janssen commenced his preparations to observe it. Unfortunately, before they were completed Paris was besieged by the German Army. Under these circumstances the British Eclipse Committee, who had invited Janssen to join their expedition, begged the intervention of the Foreign Office. Lord Tenterden

took the greatest interest in the affair, and ultimately Prince Bismarck granted a passport for Janssen to pass through the German lines with his instruments. It is not quite clear whether this ever reached Janssen, but in any case he did not take advantage of it.\* He left Paris in a balloon, the "Volta," with a single mariner as companion, on December 2. It was his first ascent, and was not without its difficulties; the proper "balancement du ballon" was not easy to secure. All, however, turned out well so far as getting to his appointed station went; but for him, as for most of the English and American observers, work was prevented by clouds.

In spite of his lameness, a good part of the next year was spent in long voyages: in 1871 to India to observe another eclipse, in 1874 to Japan for the Transit of Venus, and in 1875 to Siam, to observe still another eclipse. While at home he continued his spectroscopic observations, and, in relation in particular to the Transit of Venus, he developed the application of photography with the idea, as he expressed it, "*la plaque photographique sera bientôt la véritable rétine du savant.*" The "*revolver photographique*," then designed by him to automatically obtain a rapid succession of instantaneous pictures of Venus transiting the sun's limb, is the origin of the now well-known cinematograph.

The progress of solar studies carried on by Janssen and others had been so immense that the French Government decided to establish an observatory for solar physics. M. Duruy, the Minister of Public Instruction, first took up the question in 1869, and the Pavillon de Breteuil was granted by the Emperor for the purpose; but then came the war of 1870, and it was not till July 22, 1874, that the proposal was laid before the National Assembly to create near Paris a special observatory for astrophysical inquiries. The Minister submitted the proposal to the Academy of Sciences (August, 1874), which body not only expressed their entire adhesion to the project but strongly urged its prompt realisation. There was a provisional installation in Montmartre (Boulevard Ornano) from 1876 to 1879, until the question of site was settled. The choice lay between the two State domains of Malmaison and Meudon. The latter, still occupied by the troops, was ultimately determined upon. As the château had been burnt after the war, Janssen installed the instruments in the dependencies (October, 1876), where, indeed, he

\* On this point Madame Janssen has been good enough, in reply to an inquiry, to send me the following information:—

"Monsieur Janssen a eu connaissance des démarches faites par votre Gouvernement pour obtenir de M. de Bismarck son libre passage, mais il ne pouvait moralement en profiter; ayant reçu du Général Trochu et de Jules Simon la mission verbale d'aller trouver Gambetta à Tours où siégeait le Gouvernement de la défense nationale, il s'empresse de partir sans attendre la réponse de M. de Bismarck. Mais il n'en est pas moins resté, croyez le bien, infiniment reconnaissant au Gouvernement Anglais dont il a toujours éprouvé l'estime et la générosité, et à vous-même qui aviez pris grande part dans cette affaire.

"Aussitôt, arrivé à Tours, il est allé voir Gambetta avant de se rendre en Algérie, et pendant bien des années, il ne lui était pas possible de laisser connaître les circonstances particulières de son départ."

himself lived till his death. Two years afterwards the lower part of the château was restored, and a large dome of 18·50 m. diameter erected on it, which now contains one of the largest refractors in Europe. The other instruments were erected in observatories distributed in the grounds. The divisions of the stalls in the stables, a range of buildings 100 metres long, were utilised as supports for lengthy tubes containing the gases, the study of the absorption of which formed part of the physical programme.

The first work done at Meudon was a special photographic study of the sun's surface. The instrument employed was an object-glass of 5 inches aperture, with a secondary magnifier giving images from 12 to 18 inches diameter, using the light near the solar line G and exposures from 1/1000 to 1/3000 of a second. The photographs thus obtained were a revelation, and enabled Janssen to largely increase our knowledge of the currents in the sun's atmosphere.

On the experimental side, Janssen returned to his inquiries as to the origin of the telluric bands, this time with special reference to oxygen, and the long tubes to which attention has been called were utilised in the research. The carrying out of these and allied branches of work took some five years after the installation of the observatory at Meudon. It was not till 1882 that we find him taking part in another series of long voyages: 1882, to observe the transit of Venus at Oran; 1883, to observe still another solar eclipse on Caroline Island in the Pacific; 1884, to plead for a neutral meridian at the International Conference at Washington. On his way back from Caroline Island he repeated his spectroscopic observations at Santorin by touching at the Sandwich Islands to investigate Mauna Loa. In the emanations from the lava lake he detected spectroscopically sodium, hydrogen, and hydrocarbon vapours.

His voyages for some time onwards from 1888 had for one main object the continuance of his investigations into the bands of oxygen in the red end of the solar spectrum experimentally studied at different pressures at Meudon. In the early observations at Geneva and Nyon it was a question of water vapour, and that point was settled; but with regard to the oxygen bands it was necessary to deal with as little of the earth's atmosphere as possible, and therefore to make observations of the sun's spectrum at a great altitude. In spite of his lameness we find him doing this work at the Grands Mulets in 1888. Here he found the bands less intense; and Janssen's way was to endeavour to carry on the work in an observatory higher still, and for this nothing less than the highest point in Europe, that is, the summit of Mont Blanc itself, nearly 1800 metres higher than the Grands Mulets, would satisfy him. Thanks to the munificence of M. Bischoffsheim, the founder of the Nice Observatory, Prince Roland Bonaparte, M. Eiffel, and of Janssen himself, a Mont Blanc Observatory was determined upon in 1890, and was erected by 1893, in which year, and again in 1895, Janssen was carried up the mountain in a special form of *chaise à porteurs*. The labours of himself and others were rewarded by the result of the observations.

The oxygen bands were at their feeblest at the greatest height, and it was, therefore, the atmosphere of the earth and not of the sun which gave rise to them.

His last eclipse expedition was to Spain in 1905; his last journey was to observe the eruption of Vesuvius in 1906, when he was eighty-two years of age. His last visit to England was to take part at a Meeting of the Solar Union at Oxford, in the autumn of 1905, at which he was elected President d'honneur. His last appearance was at another Meeting of the Solar Union, held at his invitation at Meudon, in May, 1907.

The preceding account of Janssen's various activities will have shown that in his death the world of Science has lost a man of the first order. Imagination, persistence, unflagging energy, and height of aim were always present; but to those who knew him best, both in his laboratory and in the world among his confrères, his beautiful nature overshadowed his scientific reputation. He was never so happy as when descanting on the successes of his brother pioneers in the new field of work which he had been among the first to till. For him there was no question of personal achievement, the advance of knowledge, by whomsoever made, was his chief desire and delight. With such qualities of mind and heart, his declining years were made very easy for him; the devoted affection of his wife, who accompanied him in many of his voyages, and daughter, shielded him from all cares and anxieties in his modest home in one of the dependencies of the château, while the visits of affectionate friends kept his life bright. The French Government suspended their retirement rule in his favour, so that he was enabled to breathe his last in the observatory he had founded and made famous.

Janssen died full of honours. He was Commander of the Legion of Honour; he was elected a Membre de l'Institut in 1873; he was the oldest Member of the Academy of Sciences, having succeeded Laugier. He was also a Member of the Bureau des Longitudes, and had received the Lalande Medal. The Academies of Rome, St. Petersburg, Brussels, and Washington, and the learned societies of many countries enrolled his name on their list of Fellows. In this country he was a Foreign Member of the Royal Society (1875), from which he received the Rumford Medal for his researches in 1877; Edinburgh made him an LL.D. of that University, and in 1872 he was elected an Associate of the Royal Astronomical Society. He also received the Gold Medal of the Royal Geographical Society for his many voyages. This he afterwards had melted down, and from the proceeds founded an annual prize which bears his name at the Société de Géographie.

He died December 23, 1907, and was buried in Père-la-Chaise.

Wolf, Radan, Deslandres, de Lapparent, Pector, de Fonvielle, le Commandant Paul Renard, and Dr. Faveau de Courmalles, representing various scientific organisations, each pronounced a discourse over the grave.

N. L.

## THOMAS ANDREWS, 1847—1907.

THE late Mr. Thomas Andrews was born in 1847, and educated at Broombank School, Sheffield. He studied chemistry under the late Dr. Allen, and early showed a deep interest in scientific research. He was also trained in practical metallurgy and engineering under his father, upon whose death, in 1871, he became proprietor of the Wortley Ironworks.

Mr. Andrews took up the investigation of scientific metallurgy at a time when workers in this field were comparatively few, and up to the time of his death devoted a large portion of his time to scientific research. The results of these researches are embodied in forty papers, published in the Proceedings of the Royal Societies of London and Edinburgh, the Minutes of the Institute of Civil Engineers, the Proceedings of the Society of Engineers, and other Scientific and Engineering publications. As a result of these investigations, Mr. Andrews acquired the reputation of an expert upon metallurgical questions; he was consulted by His Majesty the late King of the Netherlands, the Board of Trade, the Admiralty, and many leading railway and naval companies, upon matters relating to iron and steel, and in the course of this work examined and reported upon many serious accidents caused through the breakage of steel.

Mr. Andrews was one of the first to take up the microscopic examination of metals, and contributed many papers upon this subject, paying particular attention to the crystalline structure of iron and steel, and the manner in which sulphide of manganese was distributed in steel forgings.

Previously he had exhaustively studied the corrosion of metals, and the action of tidal streams upon iron and steel. He advanced proof to show that metals which were strained or distorted by cold work were less liable to be acted upon by sea water than in their ordinary or soft condition.

Another long and costly series of experiments was made upon the effect of temperature on the strength of axles. In these experiments over 300 tons of snow were used in the making of freezing mixtures, and no less than 286 railway axles and forgings, weighing more than 41 tons, were tested and destroyed in the various experiments.

The following were Mr. Andrews' general tentative conclusions in the foregoing investigation:—

1. The impact tests with an "energy" of 10 foot-tons on axles at a temperature of 212° F., compared with results at 7° F., indicated an increase of endurance at the higher temperature of about 235 per cent.

2. The impact tests with an "energy" of 15 foot-tons on axles at a temperature of 120° F., compared with results at 7° F., showed an increase of endurance at the higher temperature of nearly 120 per cent.

3. The impact tests with an "energy" of 10 foot-tons on axles examined at a temperature of 100° F., when contrasted with results obtained at 7° F.,

demonstrated an increase of resistance at the higher temperature of about 43 per cent., and this increase was, within certain limits, in proportion to the increase of temperature.

4. The impact tests with an "energy" of 5 foot-tons on axles at a temperature of 100° F. gave an increase of resistance of about 138 per cent., compared with the results on axles similarly tested, but at a temperature of 0° F.

5. The impact experiments with an "energy" of 2½ foot-tons applied to axles at a temperature of 100° F., compared with experiments at 0° F., showed an increased resisting power to concussion at the higher temperature of nearly 88 per cent.

Another series of delicate physical experiments dealt with the electro-chemical and magnetic properties of iron and steel, and the so-called "passive state" of these metals.

A few years ago Mr. Andrews gave a course of lectures to the engineering students of the University of Cambridge upon the microscopic examination of metals, and its relation to engineering, which led to several important researches being undertaken in the University laboratories. Mr. Andrews took a deep interest in Technical Education and was a Governor of the Sheffield Technical School for many years. He also was keenly interested in the foundation of the New University of Sheffield, and, as a member of the Council, took an active part in the development of the University.

Mr. Andrews had been in failing health for the past two years, but up to the time of his death on June 19, 1907, was able to take an active interest in his metallurgical and educational work.

In recognition of the value of his work he was awarded the Telford Medal and three Telford Premiums by the Institution of Civil Engineers, the Bessemer Gold Medal, Bessemer Premium, and the Society's Premium of the Society of Engineers, and the Medal of the Franklin Institute.

Amongst his many papers the following, perhaps, may be cited as the most important, viz. :—

"Galvanic Action between Wrought Iron, Cast Metals, and various Steels during long Exposure in Sea Water," *'Min. Proc. Inst. C. E.,'* vol. 77, 1883-4.

"Corrosion of Metals during long Exposure in Sea Water," *'Min. Proc. Inst. C. E.,'* vol. 82, 1884-5.

"The Relative Electro-chemical Positions of Wrought Iron, Steels, Cast Metals, etc., in Sea Water and other Solutions," *Roy. Soc. Edinburgh.*

"Effect of Temperature on the Strength of Railway Axles," Parts I, II, III, *'Min. Proc. Inst. C. E.,'* vols. 87, 94, 105.

"Effect of Chilling on the Impact Resistance of Metals," *'Min. Proc. Inst. C. E.,'* vol. 103, 1890-1.

"Microscopic Internal Flaws in Steel Rails and Propeller Shafts," *'Engineering,'* January 17, 1896.



"Microscopic Effects of Stress on Platinum," 'Proc. Roy. Soc.,' vol. 70, 1902.

"Effect of Segregation on the Strength of Steel Rails," Soc. Engineers, 1902.

"Microscopic Structure of Gold and Gold Alloys," 'Engineering,' 1898.

"Electro-Chemical Effects on Magnetising Iron," 'Proc. Roy. Soc.,' vols. 42, 44, 46, and 52.

"The Micro-Metallography of Iron," 'Proc. Roy. Soc.,' vol. 58.

J. E. S.

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LIEUTENANT-GENERAL SIR RICHARD STRACHEY, G.C.S.I.,\*  
1817—1908.

THE Strachey family was originally settled at Saffron Walden, but in the seventeenth century they moved to Sutton Court, Somerset, their present seat. For generations many members of the family have been remarkable for their varied ability, but the name is best known from the Stracheys who have filled important civil and military posts in India. For nearly a hundred and fifty years there has never been a time without a Strachey in some important position there. Amongst these may be mentioned Sir Henry Strachey, the first baronet of the family, who was Secretary to Lord Clive, and Sir John Strachey, the celebrated Indian Finance Minister, who died only a few months before his elder brother, Sir Richard.

Richard Strachey was a grandson of the first baronet, being the third son of his second son, Edward, of the Bengal Civil Service. He was born at Sutton Court on July 24, 1817. In 1834 he entered the Indian Military Academy at Addiscombe, and two years later he left it at the head of his class, with a commission in the Bombay Engineers. On reaching India he served for a short time at Poona, and in 1839 he was transferred to the Bengal Engineers. In the following year he was posted to the Jumna Canal, one of the first large irrigation works undertaken by the Indian Government. He was next transferred to Hurdwar as executive engineer of the Ganges Canal, which had been begun in 1842 by Sir Proby Cautley. This peaceful work was interrupted by the first Sikh War (1845-6), and Strachey was posted to Sir Harry Smith's division. At the Battle of Aliwal (January 28, 1846) his horse was shot under him. He made the authoritative plan of the Sikh position before the decisive Battle of Sohraon (February 10), and assisted in the construction of the bridge across the Sutlej, whereby the British troops entered the Sikh territory. He received his brevet majority for these services, and, when peace was made, returned to his work on the Ganges Canal. But frequent attacks of fever compelled him to go to the

\* In this article free use has been made of the obituary article in the 'Times,' even where the exact words are not quoted. The author has also made use of articles in 'Nature,' in the 'Geographical Journal,' and of letters in the 'Spectator'; he has further relied on his own private knowledge and correspondence.

hill station of Naini Tal, a retirement which led to some interesting scientific work, to which we shall refer later.

After a short period of irrigation work in Bundelkhand, Strachey became in 1856 Acting Secretary to Government in the Public Works Department. In the great convulsion of the Indian Mutiny in the following year all peaceful work was naturally in abeyance, and when Mr. (afterwards Sir) John Peter Grant was placed in charge of the provisional government of the Central Provinces, with headquarters at Allahabad, he chose Strachey as his Secretary in all departments of Government.

Subsequently Lord Canning himself came to Allahabad, and Grant went to Calcutta to take up another post. Strachey, however, still remained at Allahabad, and was occupied in the restoration of that city, which had suffered much in the Mutiny. His ability was by now universally recognised in India, and he acted for a time in Lord Canning's Government as Secretary of Public Works, on behalf of Sir Henry Yule, although his actual official title was Consulting Engineer for Railways.

"In 1866 he became the first Inspector-General of Irrigation, a post he vacated three years later to resume his old post of Secretary for Public Works. Altogether for more than twenty years he exercised a commanding influence on the policy and administration of this important department, and a very strong one on the general administration. . . . 'It is to him,' wrote his brother Sir John, a few years ago, 'that India owes the initiation of that great policy of the systematic extension of railways and canals, which has been crowned with such extraordinary success, which has increased to an incalculable extent the wealth of the country, and has profoundly altered its condition.' . . . The story is told that, when he took the first of the famous despatches, defining his policy and pressing it upon the Secretary of State, to Lord (then Sir John) Lawrence, the Viceroy read it through carefully without a word, put his initials at the foot, and remarked with a shake of the head, 'Strachey, they will think me very clever.'"<sup>\*</sup>

In laying out the system of Indian railways, there was a hot controversy as to the gauge to be adopted, and Strachey advocated the adoption of a narrow-gauge for thinly inhabited tracts of country. This plan was followed, although he foresaw that in many cases the narrow might ultimately need conversion to the broad gauge. In a memorandum written for the Duke of Argyll after his return from India he pointed out the superiority of the narrow gauge for military purposes. A distinguished colleague of his on the Indian Council is still of opinion that, on this question of the gauges, Strachey was wrong.

On such questions he was accustomed to argue eagerly, and perhaps in too masterful a spirit; but he was incapable of any resentful feeling when opposed, and his generous nature led him to be fair-minded in all his dealings.

On Strachey's leaving India in 1871, Lord Mayo's Government took the

<sup>\*</sup> The 'Times,' February 13, 1908.

unusual course of thanking him for his valuable services, and on his return to England he was appointed Inspector of Railway Stores at the India Office. In 1875 he was nominated by Lord Salisbury to the Indian Council, and in 1876 he retired from the army with the rank of Lieutenant-General.

Although he had retired from permanent office in India he returned there in 1877 on a mission connected with the purchase of the East Indian Railway by the Government and remained until 1879, having been appointed President of the Famine Commission, and subsequently temporary Finance Minister in place of his brother Sir John.

In connexion with this stage of Strachey's Indian career, it may be well to quote portion of the eloquent appreciation by Sir Charles Elliott contained in a letter addressed to the '*Spectator*,'\* for this letter shows how his personality and his work were esteemed by one of his most distinguished colleagues. The letter is as follows:—

"I venture to offer what must be an inadequate tribute to the great achievements of Sir Richard Strachey. It cannot be an adequate tribute, for one of the most remarkable things about him was the varied and many-sided character of his gifts. Beginning as a brilliant soldier in the Sikh War, he rose to the summit of his profession as an engineer in the construction of irrigation canals and railways, and in defining the policy which should govern the programme of their extension. He held a leading position as a man of science in respect of botany, meteorology, geology, and geography; and towards the close of his Indian career he showed qualities of the highest statesmanship in dealing with the questions of famine policy, and with the problems of finance and exchange, when the fall in the price of silver threatened to plunge India into an abyss which would engulf the whole of the growth of her revenues. I doubt if anyone exists who is competent to deal with all the various and complex facets of such a mind, and I at least can only speak on what came under my own observation during the time when I was fortunate enough to be brought into close connexion with him.

"When the first Indian Famine Commission was appointed in 1878, with Sir Richard Strachey as President, I became its Secretary, and during two years, one of which was spent in making inquiries in India, the other in drawing up the Report in England, I was in intimate communication with him. He had long been deeply interested in the subject, and in the famine of 1868—69 had drawn up for his brother a paper which Sir John, who was then Magistrate and Collector of Moradabad, fully adopted, and which embodied the rudiments of the main lines of policy which the Commission's Report more fully developed. The system which it laid down as to the proper measures for famine relief has been tested by the two severe famines of 1897—98 and 1899—1900, and has in the main held its ground. The recommendations as to administrative changes, the creation of the Agricultural Department, the great activity of the Forest Department

\* February 22, 1908.

" (a Department in the creation of which he had taken a leading part), the  
" prosecution of public works for the protection of the country against  
" drought, and the encouragement of diversity of occupations have been or  
" are still being carried out, and have been productive of immense good to the  
" country."

In 1889 Strachey resigned his life-tenure of membership of the Indian Council, to which he had been appointed by Lord Cranbrook, in order to take up the Chairmanship of the East Indian Railway. Under his leadership the mileage of the East Indian Railway rose from 1600 to 2700 miles, and it became one of the most prosperous railways in the world. The salary attached to the office was insignificant compared with that received by the chairmen of other great railways. It should be mentioned that Strachey was also Chairman of the Assam-Bengal Railway, and that he only resigned these positions in 1907, when nearly ninety years of age.

Sir Arthur Godley, Permanent Under Secretary of State, who enjoys an exceptional position for reviewing the careers of the men who have played important parts in Indian administration, writes thus of Strachey's services at the India Office\* :—

" It is difficult to convey an idea of my opinion of them without seeming to  
" exaggerate. He was not only invaluable in his own special lines of Public  
" Works and Finance, but his knowledge and his interests were universal ; there  
" was no department of our work on which I was not always glad to get his  
" opinion, especially if the subject was one of any difficulty or anxiety. His  
" extraordinary ability and insight, his immense knowledge of everything  
" relating to India, his wonderful industry and power of work, his absolute  
" 'straightness' and fearlessness in giving his opinion—these things give him,  
" in my official memory, a place apart ; I have known many first-rate public  
" servants, but I never knew one quite like him in all these respects."

The great career which has been thus sketched would seem to be more than sufficient to fill the life of one man, and yet no mention has been made of that part of his activity which leads to the notice of his life in these pages. It seemed best to separate the accounts of the official work from that of his work in science, although the two are really closely intertwined. In the letter of Sir Charles Elliott, portion of which has been already quoted, we read :—

" It is an interesting subject for reflection to consider how much India  
" owes to the constitutional delicacy of some of her greatest men. . . . No  
" one would connect Sir Richard's keen and fiery temperament with  
" disease ; but it was to a time when he was incapacitated from his canal  
" work by malarial fever that he owed his opportunity for burgeoning out  
" into the studies of botany and geography in the Himalayas, which led to  
" his honours as President of the Geographical Society and as Fellow of the  
" Royal Society."

It was in 1846, when, as already mentioned, he was compelled by frequent

\* From a private letter.

attacks of fever to relinquish his work on the Ganges Canal, that he undertook extensive explorations in the Himalayas and into Tibet. An anonymous correspondent in the 'Spectator'\* writes:—

"Starting from the plain of Rohilkand, at an elevation of about a thousand feet above sea level, a north-easterly route was taken across the snowy ranges, and terminating on the Tibetan plateau at an altitude of between 14,000 and 15,000 feet on the upper course of the River Sutlej. . . . The herbarium, which contained over two thousand species (including cryptogams); was distributed in 1852-53 to the Hookerian Herbarium (now at Kew); the British Museum, the Linnean Society, and to some of the Continental museums. All the specimens were carefully ticketed with notes of the localities and elevation at which they were found. A provisionally-named catalogue, prepared by Sir Richard Strachey, was printed, and a copy was sent with each distributed set of plants. This catalogue was afterwards printed, and appeared in 1882 in Atkinson's 'Gazetteer.' . . . . At the request of Sir Richard Strachey another revised edition was prepared by Mr. J. F. Duthie. . . . . Of the large number of new species and varieties discovered [by him] no less than thirty-two bear his name."

I learn from a letter from Sir William Thiselton-Dyer that this journey was made in conjunction with Mr. J. E. Winterbottom, who went to India in 1848 to make botanical collections, and that the Government of India recommended him to the charge of Strachey, who was then surveying in the Himalayas. The geographical and other results of the expedition were to have been worked out by Mr. Winterbottom, but he died in 1854, and his journals were lost. Strachey therefore published his own account of the journey in the 'Journal of the Royal Geographical Society' in 1900, and the botanical results were only published in 1906, after a lapse of nearly sixty years. Thiselton-Dyer considers this to be one of the most important documents in existence on the Himalayan flora.

The geological observations made by Strachey during this journey, and published by the Geological Society in 1851, afforded the first contribution to our knowledge of the geology of the Himalayas. He studied the glaciers of Kumaon, and established the existence of a great series of palæozoic beds along the line of its passes leading into Tibet, with jurassic and tertiary deposits overlying them. Sir Thomas Holdich writes:† "It is not too much to say that the information acquired by Strachey in that first excursion across the Himalayas—information geological, botanical, relating to glaciers and snowfall . . . has never been exceeded by any one traveller." In consequence of the knowledge acquired in his travels, he was invited to write the articles "Asia" and "Himalaya" in the 'Encyclopædia Britannica.'

Previously to this journey he can have had but little knowledge either of botany or of geology, and it affords a striking testimony to his ability and

\* In a letter, signed "B.," February 22, 1908.

† The 'Geographical Journal,' March, 1908, p. 343.

energy that he should have been able to obtain such important results. As a consequence of these contributions to science he was elected to the Royal Society in 1854.

On his return to England he naturally became a leading power at the Royal Geographical Society, and from 1887 to 1889 he filled the office of President. During his tenure of the Presidency he endeavoured to promote the teaching of geographical science, and he came to Cambridge to deliver a short and admirable series of lectures on the scope of geography, which were afterwards published in the form of a book. In June, 1892, the University recognised this service and his many contributions to science by conferring on him the degree of LL.D., on the recommendation of the Duke of Devonshire, Chancellor of the University, and formerly Secretary of State for India.

He also exercised great influence at the Royal Society, and served on the Council no less than four times—viz., in 1872–4, 1880–1, 1884–6, and 1890–1; and in 1880–1 and again in 1885–6 he was nominated as one of the Vice-Presidents.

He was one of the British delegates at the International Congress at Washington in 1884 for determining the Prime Meridian, and acted as one of the three Secretaries.

Great as are the services to science which have been already enumerated, we have not yet come to that branch of science to which Strachey made his most important contributions. On his return from India in 1873 he was appointed a member of the Meteorological Committee of the Royal Society, which controlled the Meteorological Office established in 1867. He was a member of Sir William Stirling Maxwell's Committee which revised the constitution of the governing body of the Office, and was a member of the Council which replaced the Committee in 1876. On his final return from India he resumed his place on the Council; on the death of Professor H. J. S. Smith in 1883 he was appointed Chairman, and he held that position until the termination of the existence of the Council in 1905 and the reorganisation of the Office on its present footing.

An article by Dr. W. N. Shaw, the present Director of the Meteorological Office, gives an admirable account of Strachey's position in meteorological science. Dr. Shaw writes as follows:—\*

"My personal recollection of Sir Richard Strachey goes back to 1880, when I was engaged upon some work for the Meteorological Council. He was keenly interested in questions about the distribution of vapour pressure in the atmosphere. The vertical distribution was the subject of a paper in the 'Proceedings' of the Royal Society in 1862. My recollection is that he had a good deal to do with disposing of an idea that I have seen attributed to Herschel, that in reckoning the pressure of the atmosphere, water vapour did not count . . . . ."

"The distribution of vapour pressure in the atmosphere as determined by

\* 'Nature,' February 27, 1908.

“ his own observations up to 18,000 feet in the Himalaya was again discussed (in the Cambridge Lectures) . . . . He returned to the subject of aqueous vapour in the atmosphere again in the determination of the heights of clouds by photographic observations at Kew ; a preliminary report on the measurements was contributed to the ‘ Proceedings ’ of the Royal Society in 1891, and there still exists a great store of unworked material.

“ From 1897 onwards I was closely associated with Strachey in the management of the Meteorological Office, and I speak without hesitation for his colleagues, Galton, Wharton, Buchan, Darwin, Field, and Scott, in saying that association with him was not the least among the privileges which attached to membership of the Council. His clear insight into the questions at issue, his perfect lucidity in thought and expression, the logical marshalling of facts in the official documents which he wrote as Chairman, will always be memorable. He had not much patience with people who were imperfectly acquainted with the facts of a case under discussion, and he never cared to argue with them, but difference of opinion on lines of policy, even when ill expressed, never ruffled his serenity in the conduct of business. From time to time while he was Chairman the office was subject to criticism which was not always fair, but he never complained. He was always content to attribute the criticism to want of knowledge of the facts. He would not even let us indulge in the semi-official pastime of abusing the Treasury. Their responsibility had to take account of an aspect of the matter with which we were not cognisant, namely, where the money was to come from, and we must be content to accept a judgment that had to reckon with public opinion in its executive form as well as with scientific aspirations. Speaking for myself as one accustomed for many years to the details of business of College meetings and University syndicates, Strachey’s methods of transacting corporate business were a revelation.

“ As regards his later contributions to the science of meteorology, some words of explanation are necessary. He had watched, and indeed had been largely instrumental in providing the facilities for its study both in India and in this country, on the new lines of the comparison of results for different parts of the country or of the world. He was conscious that the new science required a new method, that the method of the physical laboratory which aims at elucidating a physical process by experiments specially directed thereto was inapplicable to the case of the free atmosphere. Those who are critical of the vast accumulation of meteorological data which is going on are apt to be unaware of the fact that data have to be collected in advance, and that, to this day, nearly every attempt to deal with a meteorological problem of any importance is baffled by the want of data ; they are equally unmindful of another noteworthy fact, namely, that in meteorology comparison is of the essence of the science. The meteorologist is absolutely dependent upon other people’s observations ; his own are only useful in so far as they are comparable with those of other people. Thus the time, trouble, and money spent upon organisation are not the expressions of limited scientific ambition, but a

“primary condition for securing indispensable facilities. Strachey’s scientific judgment was extraordinarily acute. He was quite prepared to carry on investigation to a speedy issue when circumstances permitted, as in the investigation of the Krakatoa eruption, which led to the recognition of a westerly drift in the upper air of the equatorial regions as a primary meteorological datum.”

The paper to which Dr. Shaw here refers is Strachey’s admirable contribution to the volume of the ‘Philosophical Transactions’ of 1888, on the barometrical disturbances and sounds produced by the eruption of Krakatoa. To revert to our quotation:—

“In dynamical meteorology he was convinced that the most promising mode of attack was not to look for a direct dynamical explanation of the striking features, the eccentricities of the day’s weather, which are the almost fortuitous result of many causes combined in various phases, but to seek for the relations between regular sequences and their causes underlying the apparently arbitrary variations. For this reason the methods of harmonic analysis specially attracted him, and he was disposed to regard anything less general than five-day means as unmanageable. He never completed the work on harmonic analysis that he had in hand. He attached particular importance to the third Fourier component of diurnal variation, because the length of the day in these latitudes oscillates between one-third and two-thirds of the twenty-four hours. A few years ago he took up again the investigation of the question, and he has left a considerable amount of unfinished material.

“He was not to be driven from a position of modest optimism about such matters, and always explained that for a new science the progress made in the last fifty years is quite as great as could fairly be expected.

“But he was no friend of the unnecessary compilation of data or of the unlimited extension of mean values. Almost the last contribution that he gave me was a computation of the number of years necessary to reach a mean value for temperature within the limits of the probable error of the mean value for a single year, based upon some tables published in 1902 for the extrapolation of mean values. He was always more concerned to present meteorological data in a form amenable to computation than to increase their volume or detail. When the weekly weather report was initiated in 1884, he provided formulæ for computing the true daily mean from the maximum and minimum temperatures for the day, and for computing the amount of effective and ineffective warmth as referred to a base temperature of 42° F., which are still in use. He once astonished me by pleading for graphical representation as being easier to read than columns of figures, for he could extract the meaning of a page of figures with a facility that made the discussion of results with him an indispensable part of any piece of work that was in hand. Yet he was more than eighty years of age when we had to transact this kind of business together. He never lost his appreciation of new methods which were sound, or of new projects which were promising.



“ Throughout his administration of the office he held to a high scientific ideal while maintaining the efficiency of such daily work as was required for public use and for international co-operation. His scientific horizon was a wide one. With Stokes and Balfour Stewart he was largely instrumental in providing means for the organised study of the sun, which had been commenced in this country and in India by Sir Norman Lockyer, in order to trace the primary causes of those great meteorological fluctuations which exhibit themselves in alternations of drought and plenty in India, a study which, pursued for many years at the Solar Physics Observatory at South Kensington and at Kodaikanal, in India, has recently taken its place among the greater international organisations. As head of the Public Works Department in India he transferred meteorological work in that dependency from a provincial to an Imperial basis under Blanford and Eliot, and laid the foundation for the admirable organisation of which the Government of India and its scientific staff now enjoy the advantage. At the same time he initiated the forestry department, and the application of botanical science to the service of the public in that department.

“ Probably no single person had clearer views of the future that lies before meteorological work as a matter of practical influence upon everyday life, or was more fully conscious of the long years of observation, organisation, and study that are necessary to secure the advantages which will ultimately more than reward the long years of patient inquiry.”

On his retirement from the Meteorological Council in 1905, his colleagues on the Council addressed a letter to him expressive of their sense of the advantages which had been secured to the meteorological service of the country by means of his Chairmanship of the Council. In his acknowledgment he wrote thus:—

“ The exceptional difficulties that surround the scientific treatment of the subjects which the Council has had to consider have been further increased by the restricted means at our disposal for dealing with the great diversity of the objects that called for attention; and it is no small satisfaction to me to feel that it has been possible for us to do so much, and to maintain a scientific level that is, to say the least of it, in no way below the standard attained by similar institutions in other countries carried on under far more favourable conditions.

“ The success thus secured is certainly due in no small measure to the hearty co-operation of all the members of the Council and their Secretaries, supported as they have been by a highly intelligent and devoted staff, several of whom have been connected with the Office from the time of its original constitution.

“ Conscious as I am of my personal limitations, I thank you most sincerely for the generous appreciation you have accorded to my efforts, and specially for recalling my association in the work of the Council with the former eminent members whom you have named. To these I may be allowed to add two of our distinguished retired members, Francis Galton,

“ to whose fertile genius meteorological science owes so much, and Admiral “ Wharton, through whom the active association of the Hydrographic Department of the Admiralty with the Marine branch of the Meteorological Office “ has been so greatly promoted.”

In 1866 Strachey was made a Companion of the Star of India, and in 1897 he was advanced to the highest grade of the Order, the Grand Commandership. In the same year one of the Royal Medals of the Royal Society was awarded to him for his researches in physical and botanical geography and in meteorology. Finally, in 1906, he received the Symons Medal of the Royal Meteorological Society.

After his return from India he lived for some time at a house with a charming garden, called Stowey House, on Clapham Common. Later he moved to a house in Lancaster Gate, and, only a few months before his death, he again removed to a house at Hampstead. Almost every summer he was accustomed to take a furnished house somewhere in the country, usually in one of the home counties. Although these times were nominally holidays to be enjoyed with his family, he still did much work, and usually attended various meetings in London. During the last two or three years he had several severe illnesses, and on one occasion, when nearly eighty years of age, he was knocked down by a cab in the streets of London. His excellent constitution enabled him to rally wonderfully on these occasions, and he was soon at work again. After he gave up all his many positions, and when he became less vigorous in health, he principally devoted himself to reading novels, but his mind remained wonderfully fresh to the end, so that he still took an interest in all that was going on in the world. His final illness was an attack of influenza, from which he had not sufficient strength to rally. He died on February 12, 1908, being then nearly ninety-one years of age. A memorial service, held at Christ Church, Lancaster Gate, was largely attended by many of his old Indian colleagues, and by representatives of many of the learned societies.

Although no attempt has been made in this article to speak of Sir Richard Strachey's family life, it is proper to mention that in 1859 he married Jane, daughter of his old chief, Sir John Peter Grant, of Rothiemurchus, who survives him. He leaves also five sons and five daughters.

He was in stature slightly below the middle height, and was somewhat shortsighted. His appearance was striking, and he always retained the look of a soldier; in conversation he was invariably interesting, and one could not fail to be impressed by the vigour of his common sense and by the incisiveness of his views. It was a privilege to know one who combined in so rare a degree the practical energy of the great administrator and the insight of the man of science.

G. H. D.



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